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L.K. Pleijsier (ed.)

25-29 August 1986
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PROCEEDINGS
of an
INTERNATIONAL WORKSHOP
on
The LABORATORY METHODS and DATA EXCHANGE PROGRAMME

edited by
L.K. Pleijsier

25 - 29 August 1986
Wageningen, The Netherlands

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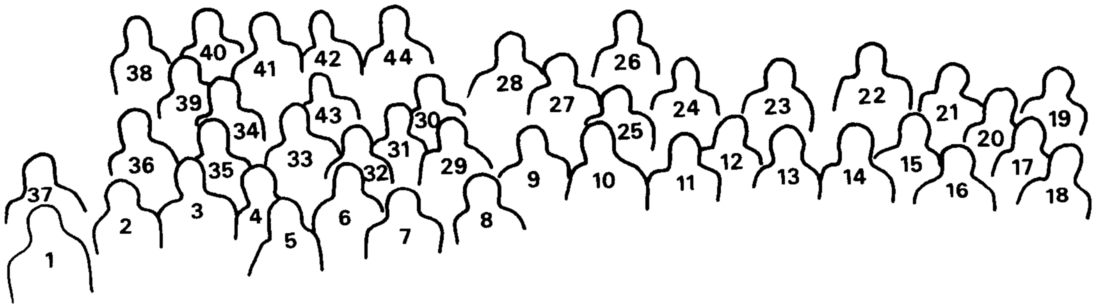

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INTRODUCTION

W.G. Sombroek
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On behalf of the LABEX secretariat and the other ISRIC staff I welcome you at this first international workshop on 'The Laboratory Methods and Data Exchange Programme'.

I am happy to note that so many specialists engaged in soil analysis are able to attend, demonstrating their large interest in the subject matter. This Labex meeting was deliberately planned the week after the ISSS congress at Hamburg to enable attendants to combine their travel. I think that this has been succesful as I see many of you, whom I did see last week at the Congress.

Why do we have the LABEX programme and why do we have this workshop? International systems of soil classification and correlation have become more and more accepted in recent years, e.g. the FAO/Unesco system and the USDA Soil Taxonomy. International soil correlation implies international exchange of analytical data, and this requires international comparability of data. Another aspect of the Labex programme is the quality control. By offering reference samples the individual participating laboratories can assess their performance and improve the quality of their work.

The necessity of this exchange of samples and data was recognized already fifty years ago. In 1936 the ISSS-congress at Oxfore charged Dr. D.J. Hissink (Institute of Soil Science, Groningen, the Netherlands), 'to collect and distribute a set of reference soil samples for comparative studies in the domain of exchangeable bases' (see also ISSS Bulletin no. 69, 1986/1). In 1978 the 2nd International Soil Classification Workshop held in Malaysia and Thailand expressed in one of its resolutions that 'laboratory methods for soil characterization in various parts of the world be cross-checked, correlated and if possible standardized and that the ISRIC in Wageningen assume an active role in this matter'. This recommendation was strongly supported by Unesco's ad-hoc Advisory Panel to ISRIC in 1979. Shortly thereafter, to comply with these recommendations, ISRIC initiated such a cross-checking project through a pilot phase in which 20 soil laboratories participated. Already during this pilot phase much interest was shown by other soil institutes. Thanks to a research grant for 2.5 years from the Dutch Government's Directorate General for International Cooperation the Labex programme could be expanded to full scale from 1st January 1985. At present the number of participants is nearly 90, though not all equally active.

We are grateful to the ORSTOM of France and the USAID-SMSS of the U.S.A. for the support they have given to the organisation of the workshop. This enabled us to invite more participants than otherwise would have been possible. I hope that during this workshop you will make it clear whether you want the Labex programme to continue, and if so, how you want it to continue. This workshop is meant to be a means of communication, among the Labex participants and between the secretariat and participants.

I hope that this will contribute to our aims: the improvement of soil analysis, for soil classification and correlation, and for more efficient use of fertilizers.

I wish you a most successful workshop.

THE LABEX PROGRAMME AND ITS RESULTS SOFAR

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I Introduction

The Labex programme was initiated on recommendation of the 2nd International Soil Classification Workshop in 1978. It had become clear at that moment that international classification and correlation of soils were hampered by the poor standardisation of analytical methods, leading to a large variability in analytical results. Therefore the Labex programme was initiated as a laboratory cross-checking programme with the aim to investigate the possibilities of standardization. For each relevant soil parameter a universal analytical procedure was to be established that could be incorporated in international soil classification systems.

II Sources of variability

When making a chemical or physical analysis we try to determine the numerical value of a parameter. This parameter has a 'true value' (although sometimes varying with conditions, e.g. CEC depends on pH) which is usually unknown. In practice the analytical results are scattered around this true value. 'Precise' results are scattered close together but not necessarily around the true value, while 'accurate' results are scattered around the true value but not necessarily close together. In Fig. 1 the concepts of precision and accuracy are illustrated. Precise results show a certain 'bias'. In Fig. 2 three clouds of data represent the results of three laboratories. The expected difference between two results from the same laboratory is the 'repeatability' (r), while the expected difference between two results from different laboratories is the 'reproducibility' (R). Formal definitions of R and r are give in the ISO standard for collaborative studies (ISO, 1981).
- Repeatibility is defined as: 'the value below which the absolute difference between two single test results obtained with the same method on identical test material under the same conditions (same operator, same equipment, same laboratory, short interval of time) may be expected to lie with a specified probability (usually 95%)'.
- Reproducibility is defined as: 'the value below which the absolute difference between two single test results obtained with the same method on identical test material under the different conditions (different operator, different equipment, different laboratory, long interval of time) may be expected to lie with a specified probability (usually 95%)'.

The variation in the data can have various sources. Some are given in the following table.

Source of variation	within lab.	between lab.
definitions		X
procedures		X
execution of procedure	X	
instruments	X	
operator	X	
random error	X	
calculations	X	X

The variation can be divided into two components: the within-laboratory variation and the between-laboratory variation. It is the responsibility of the head of a laboratory to reduce the within-lab variation. To reduce the between-lab variation external comparisons are needed and this can be provided by cross-checking programmes such as Labex.

III Operations of LABEX

The Labex Programme sends soil samples to the participating laboratories. The laboratories analyse the samples and return the results to the Programme Secretariat. Results are then compiled in a report and distributed among the contributors of the data. Since January 1985, when Labex started as a full scale project, soil samples were mailed twice: in June 1985 and February 1986. The first batch of samples was analysed by the labs using their own 'best' method. Subsequently the labs were requested to repeat the analyses using methods prescribed by the Labex programme. The second batch of samples was also analysed using the 'Labex methods'.
This can be schematically represented as follows:

samples I ----▸ Data 85-1 : own 'best' method
↘-▸ Data 85-2 : 'Labex' method

samples II ----▸ Data 86-1 : 'Labex' method

To know the analytical methods used for the 85-1 data a questionnaire was sent with the samples. This questionnaire covered the analyses for texture, CEC and exchangeable cations, pH and organic carbon. It turned out that a wide variety of methods were used. No two methods were equal in detail.

IV Individual laboratory performance

When looking at the results two different points of view can be taken: the standpoint of the individual participant who is interested to know how his own results compare with the results of others, and the higher standpoint overlooking all data and considering them as a whole structure. The data obtained thusfar are compiled in the 'Interim Reports on the Exchange Rounds' (Pleijsier 1985, 1986a, 1986b). These interim reports serve the first standpoint. Data are compiled in synoptical tables and outliers are indicated. The clay content figures for sample 17 from 85-1 may serve as an example. This is a soil sample from a Pellic Vertisol in Kenya. From the histogram in Fig. 3 it appears that the lowest reported value is less than 2% clay and the highest reported value is nearly 90% clay. A normal curve with the same mean and standard deviation as the actual data is superimposed in the figure with dots. As the data distribution is skewed the median is a better estimate of the centre of the data than the mean. The calculations to identify outliers proceed along the following steps:

calculate per sample:
- median -----▸ MED1
- median of ABSOLUTE(values - MED1) -----▸ MAD1
- mark values > (MED1 + 2.F.MAD1) -----▸ **
  values < (MED1 - 2.F.MAD1) -----▸ **
- delete values marked with **

repeat calculations on remaining table:
- median -----▸ MED2
- median of ABSOLUTE(values - MED2) -----▸ MAD2
- mark values > (MED2 + 2.F.MAD2) -----▸ *
  values < (MED2 - 2.F.MAD2) -----▸ *

'**' and '*' refer to the earmarking of data in the tables in the Labex Reports.
In Fig. 3 the numerical values for MED1, MAD1, MED2, MAD2 and F are given. The factor F is such that had the data been normally distributed, 5% of the data would have been marked. F depends on the number of labs in the table. Values marked with '**' can be considered as outliers, while values marked with '*' are dubious. A simple evaluation of the performance of a lab can be obtained by summing the number of asterisks scored, and comparing this score with the score of other labs.

More sophisticated is the Rank-Sum-Test for outlying laboratories. In this test the actual values are replaced by their rank per sample. Per laboratory these ranks are summed. Exceptional high scores and exceptional low scores indicate consistently high respectively low values. In the Interim Reports this Rank-Sum-Test is elaborated.

A disadvantage of this test is that high ranks for some samples can be compensated by low ranks for other samples. To visualize the performance of a lab its data can be plotted against the median of all data. In Figs. 4 and 5 the data of lab 7 and lab 55 are plotted respectively. The plots of the data of lab 7 lie along the diagonal. The data of lab 55 lie almost consequently below the diagonal and also they show more scatter. This indicates that both accuracy and precision for lab 55 are lower than for lab 7.

V Global results

Now let us look at the data as a whole structure. In Fig. 6 the clay figures of sample 17 are plotted against the data of sample 18, both from the same Pellic Vertisol in Kenya. These 2 samples are related, in the sense that their behaviour is assumed to be similar. If all labs had performed ideally all would have obtained the same result for sample 17 and all would have had the same result for sample 18. All plotted points would coincide at one point S. This is obviously not the case. A lab which has high precision but low accuracy will produce data that have a certain bias, and as samples 17 and 18 are similar, this bias is assumed to be equal for both the samples. So the plot of this lab will fall on a line through point S, parallel to the diagonal. Thus the distribution along this line is related to the between-lab variance and the distribution perpendicular to this line is related to the within-lab variance. From these variances the repeatability r and reproducibility R can be calculated. These calculation procedures are given in ISO-5725. The underlying assumption in this calculation is the normality of the data. From the histogram in Fig. 3 it was already clear that this assumption cannot be made. Therefore the values of R and r cannot be taken too absolutely but should only be regarded as indicative. In Fig. 6 the calculated values for R and r are given. Also P, the number of plotted points, and M, the overall mean, are given. Another illustration of a two sample plot is given in Fig. 7. Here the two samples are nos. 25 and 26 of a Xanthic Ferralsol from Brazil.

Table 1 gives the results for the sample pairs in the data 85-1, 85-2 and 86-1. From this table it can be seen that the values for R and r are very high. The change from own 'best' method in 85-1 to 'Labex' method in 85-2 and 86-1 appeared to have little or only erratic effect on the results of R and r.
This could have had various reasons e.g.
- the 'Labex' methods were not clear or not unambiguous;
- the participating labs were not used to the 'Labex' methods;
- the 'Labex' methods were not suitable for (all) the soil samples.

To solve this last point it is perhaps feasible that the Labex programme does not stick to one 'standard' method but that methods are differentiated according to certain properties of the sample. Perhaps a tree of soil analytical procedures has to be developed:

```
soil sample  ---▶  test 1  ------▶  procedure 1
                           \
                            \--▶  test 2  ------▶  procedure 2
                                          \
                                           \--▶  procedure 3
```

Hopefully during the workshop these differentiated procedures can be identified.

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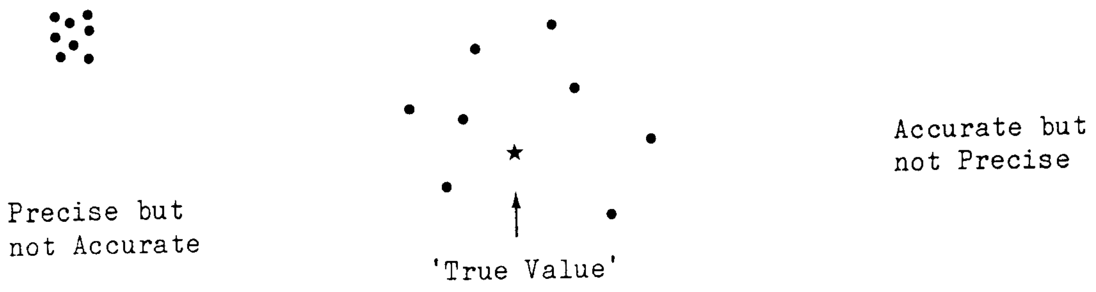


Figure 1. Concepts of Accuracy and Precision.

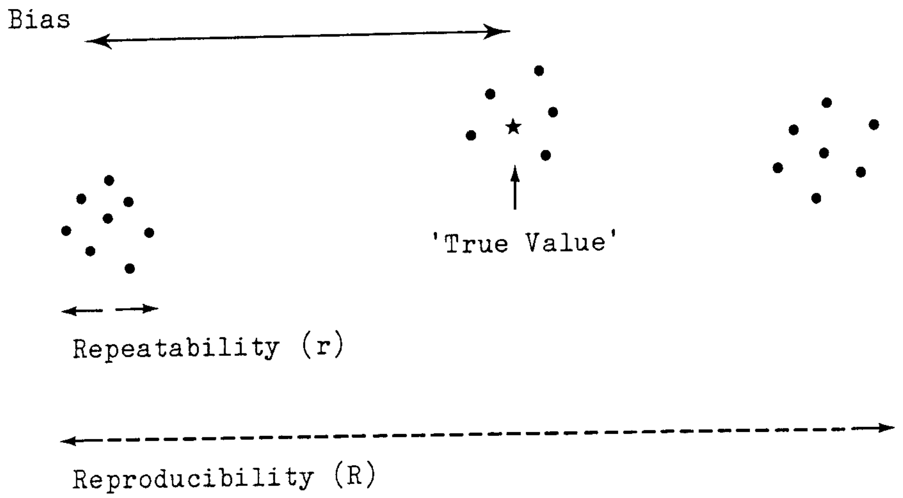


Figure 2. Concepts of 'Repeatability' and 'Reproducibility'

```
                              Count  Midpoint
                                1       1.90 ¦-----
                                0       3.90 ¦
                                0       5.90 ¦
                                0       7.90 ¦
                                0       9.90 ¦
                                0      11.90 ¦
                                0      13.90 ¦
                                0      15.90 ¦
                                1      17.90 ¦-----
                                0      19.90 ¦
                                0      21.90 ¦
                                1      23.90 ¦-----
                                0      25.90 ¦.
                                0      27.90 ¦.
                                0      29.90 ¦.
                                0      31.90 ¦.
                                0      33.90 ¦ .
                                0      35.90 ¦ .
                                0      37.90 ¦ .
                                0      39.90 ¦  .
                                1      41.90 ¦---:-
                                2      43.90 ¦---:------
                                1      45.90 ¦----:
                                2      47.90 ¦-----:----
                                0      49.90 ¦      .
                                1      51.90 ¦-----  .
                                0      53.90 ¦        .
                                0      55.90 ¦         .
                                2      57.90 ¦----------.
                                1      59.90 ¦-----      .
                                2      61.90 ¦----------  .
                                1      63.90 ¦-----        .
                                1      65.90 ¦-----        .
                                2      67.90 ¦----------    .
                                3      69.90 ¦--------------:
MEAN     ----------->           2      71.90 ¦----------    .
                                3      73.90 ¦--------------:
                                2      75.90 ¦----------   .
MED1     ----------->           4      77.90 ¦-------------:------
                                7      79.90 ¦------------:----------------------
    MED2 ----------->           9      81.90 ¦-----------:---------------------------------
                                7      83.90 ¦-----------:-----------------------
                                5      85.90 ¦----------:--------------
                                3      87.90 ¦---------:-----
                                2      89.90 ¦--------:-
                                             I....+....I....+....I....+....I....+....I....+....I
                                             0         2         4         6         8         10
                                                           Histogram Frequency
```

Mean = 71.5
MED-1 = 78.5
MAD-1 = 6.5
N = 66 ---▶ F = 1.59

MED-2 = 80.4
MAD-2 = 4.2

Figure 3. Frequency distribution of results for clay % sample 17 (data 85-1)

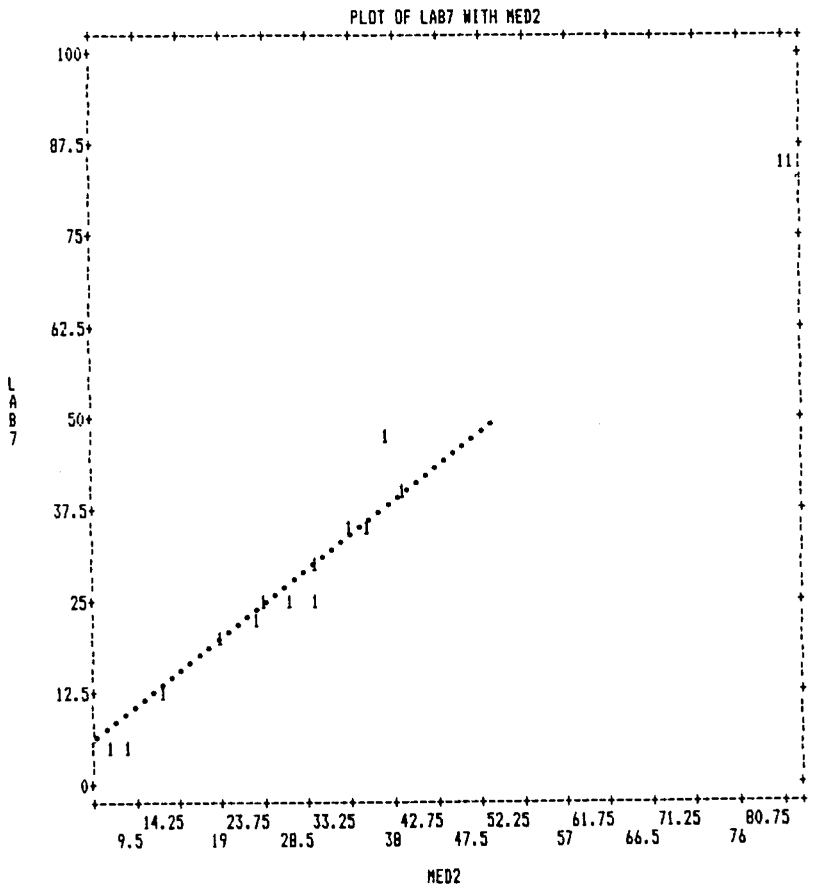


Fig. 4. Scatterplot of results
lab. 7 versus median for clay %
(data 85-1)

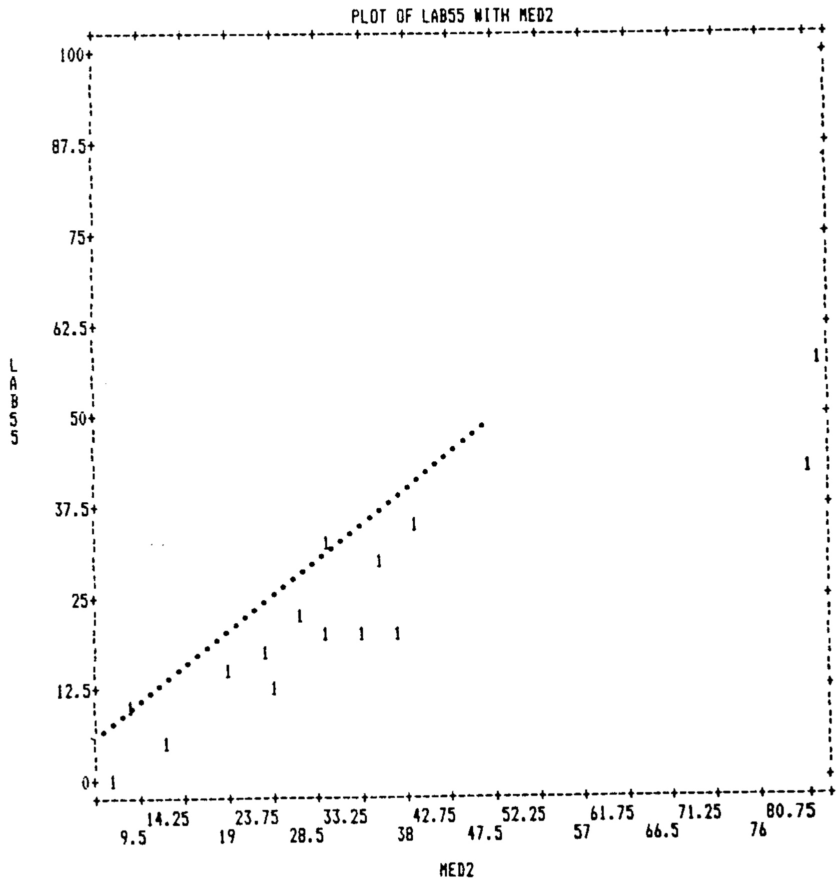
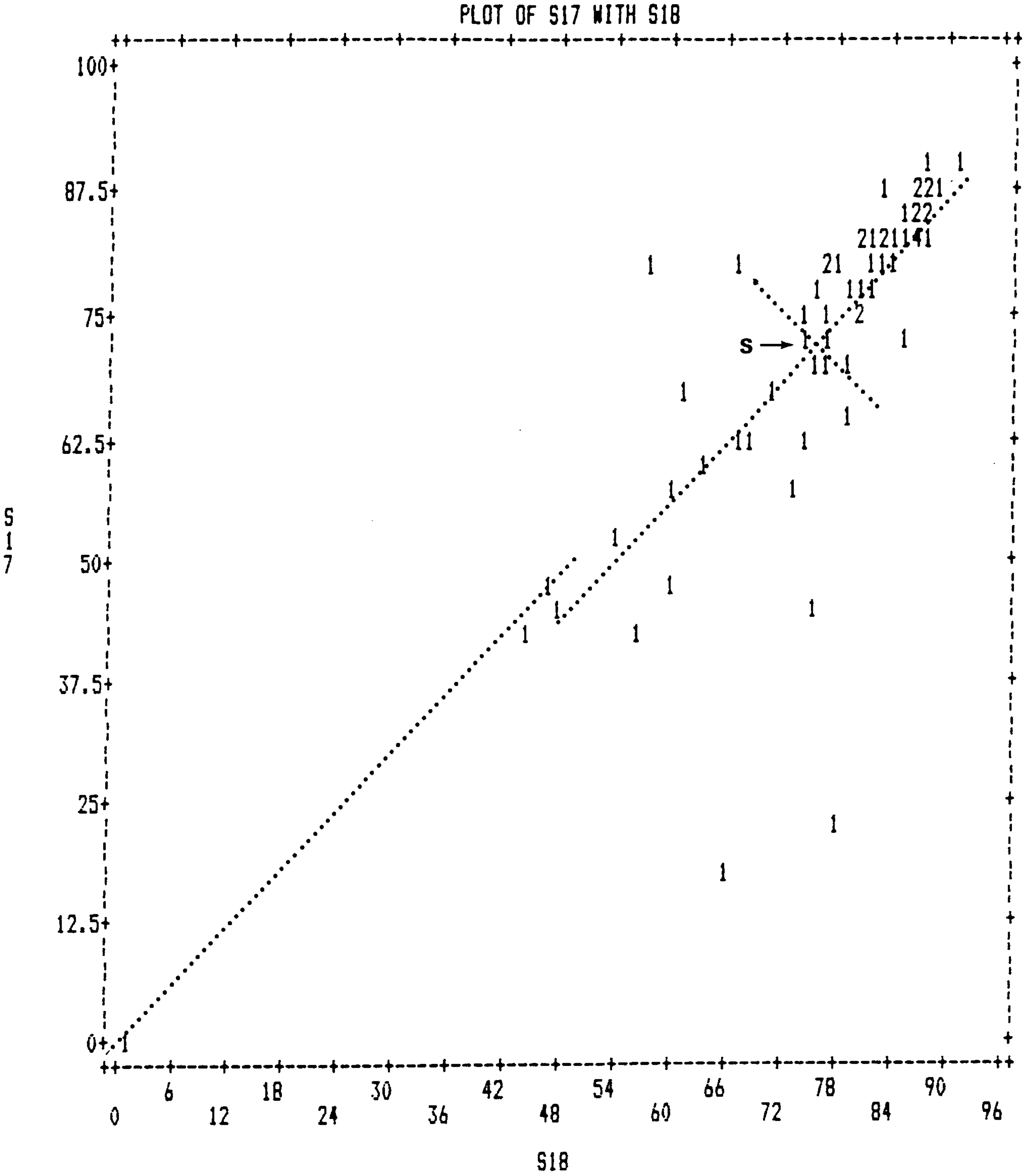


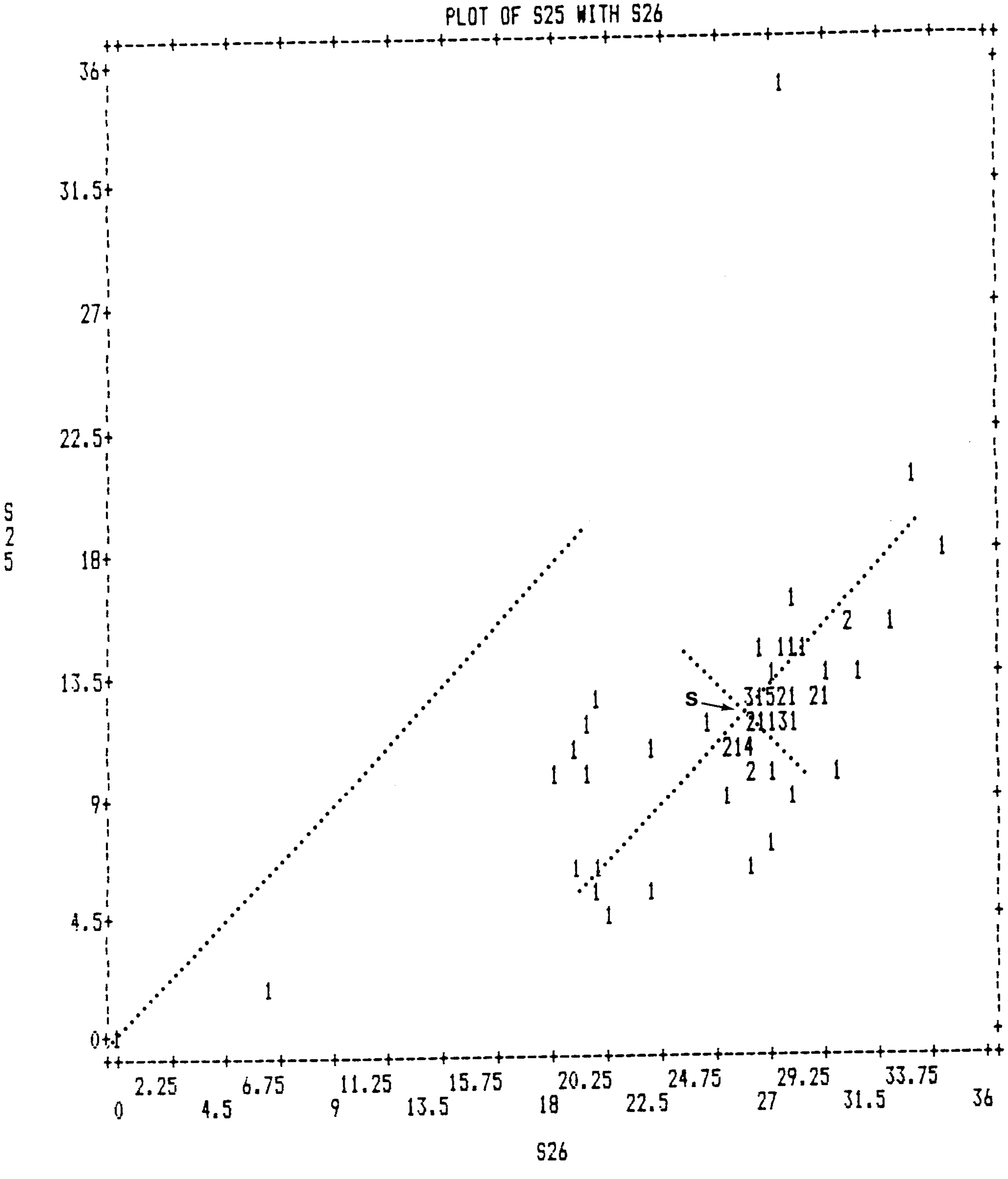
Fig. 5. Scatterplot of results
lab. 55 versus median for clay%
(data 85-1)



P = 66
M = 73.63

r = 21.15
R = 45.54

Figure 6. Two-sample-plot for samples 17 and 18, Pellic Vertisol (Kenya), for clay % (data 85-1)



P = 66
M = 18.55

r = 8.46
R = 13.64

Figure 7. Two-sample-plot for samples 25 and 26, Xanthic Ferralsol (Brazil), for clay % (data 85-1)

Table 1

Reproducibility (R) and repeatability (r) for various soil characteristics (ISO 5725)

Data 85-1

Clay

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	68	19.40	22.25	29.20	15.13	51.44	20.08
17, 18	66	73.63	207.51	57.05	21.15	264.56	45.54
19, 20	66	26.27	49.71	8.57	8.20	58.28	21.37
23, 24	65	34.73	30.74	20.21	12.59	50.96	19.99
25, 26	66	18.55	14.61	9.13	8.46	23.74	13.64
27, 28	66	21.44	25.09	13.03	10.11	38.13	17.29

pHKCl

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	57	9.12	0.12	0.03	0.47	0.15	1.07
17, 18	57	6.77	0.06	0.02	0.39	0.08	0.77
19, 20	57	5.64	0.08	0.03	0.52	0.11	0.93
23, 24	57	6.85	0.03	0.03	0.48	0.06	0.68
25, 26	56	4.71	0.06	0.03	0.52	0.09	0.86
27, 28	57	5.16	0.07	0.03	0.49	0.10	0.87

CEC

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	75	11.55	236.36	91.49	26.78	327.86	50.70
17, 18	75	73.98	321.40	69.32	23.31	390.72	55.35
19, 20	72	21.06	20.49	8.42	8.12	28.90	15.05
23, 24	73	17.46	19.62	14.36	10.61	33.99	16.32
25, 26	75	3.36	1.68	1.85	3.81	3.53	5.26
27, 28	74	11.39	6.89	1.63	3.57	8.51	8.17

OC

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	67	0.33	0.33	0.05	0.62	0.38	1.72
17, 18	67	1.58	0.08	0.11	0.91	0.19	1.20
19, 20	68	1.32	-0.01	0.09	0.86	0.09	0.82
23, 24	68	1.14	-0.02	0.10	0.87	0.08	0.79
25, 26	68	0.75	0.01	0.05	0.64	0.06	0.70
27, 28	67	0.28	0.01	0.00	0.19	0.01	0.28

P	number of sample pairs
M	mean of data
S^2_L	between-laboratory variance
S^2_r	repeatability variance
S^2_R	reproducibility variance

Data 85-2

Clay

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	41	17.22	11.56	18.96	12.19	30.52	15.47
17, 18	42	81.12	146.99	19.26	12.29	166.25	36.10
19, 20	42	28.46	11.83	11.90	9.66	23.72	13.64
23, 24	42	36.92	16.43	17.80	11.81	34.23	16.38
25, 26	41	20.09	16.01	7.00	7.41	23.01	13.43
27, 28	42	23.33	24.15	13.95	10.46	38.10	17.28

pHKCl

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	48	9.25	0.11	0.01	0.34	0.12	0.97
17, 18	49	6.74	0.11	0.07	0.72	0.17	1.17
19, 20	49	5.56	0.07	0.02	0.34	0.09	0.82
23, 24	49	6.86	0.06	0.03	0.46	0.09	0.82
25, 26	49	4.68	0.05	0.02	0.36	0.07	0.72
27, 28	49	5.11	0.04	0.01	0.23	0.05	0.61

CEC

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
15, 16	44	6.60	1.87	8.57	8.19	10.44	9.05
17, 18	44	82.45	897.28	18.70	12.11	915.98	84.74
19, 20	44	22.49	71.40	9.42	8.60	80.82	25.17
23, 24	45	17.61	41.18	10.27	8.97	51.45	20.08
25, 26	45	3.37	1.41	1.37	3.28	2.78	4.67
27, 28	44	11.60	12.04	5.54	6.59	17.58	11.74

Data 86-1

Clay

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
13, 35	39	33.83	10.33	5.43	6.52	15.75	11.11
29, 30	38	52.30	141.94	34.70	16.49	176.64	37.21
31, 32	39	71.78	121.42	59.19	21.54	180.61	37.63
33, 34	39	36.63	45.07	21.02	12.84	66.09	22.76

pHKCl

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
13, 35	46	4.15	0.02	0.01	0.28	0.03	0.48
29, 30	45	4.96	0.02	0.05	0.60	0.06	0.71
31, 32	46	4.85	0.02	0.01	0.32	0.03	0.50
33, 34	46	7.11	0.13	0.01	0.28	0.14	1.04

CEC

SAMPLES	P	M	S^2_L	S^2_r	r	S^2_R	R
13, 35	44	3.92	4.17	1.57	3.51	5.74	6.71
29, 30	44	7.64	7.50	2.30	4.24	9.80	8.76
31, 32	44	21.46	28.74	8.74	8.28	37.48	17.14
33, 34	44	32.43	67.36	717.09	74.98	784.45	78.42

CHEMICAL SOIL ANALYSES - THE REASONS FOR THEIR DRAWBACKS

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I Introduction

The use of chemical analysis as a diagnostic instrument for soil fertility and as a basis for fertilizer recommendations requires a clear understanding of its possibilities and limitations, and of how certain factors can affect quality. An ignorance of this technique's potential has caused it to be underrated and in many cases, discredited.

Obtaining accurate and precise values has always been the aim of soil analysis. Laboratory techniques have been continuously developed, adapted and improved for this purpose. However, the initial steps prior to the analysis itself - sampling, drying, grinding and subsampling - have received comparatively little attention, when facts show them to be of primary importance for generating reliable results.

The present paper analyzes the objectives of this technique in several fields, especially for soil fertility status and fertilizer recommendation. It also includes a discussion of the errors that can occurr in the phases of sampling, preparation and analysis, interpretation of results and making recommendations.

From the agronomical point of view, the main reasons for carrying out chemical soil analyses are:
a) to satisfy the demand for soil classification data;
b) to generate information for the management and improvement of soils, especially in saline areas ;
c) to determine the ecological effect of some agricultural practices, or simply the effect of environmental pollution;
d) to evaluate soil fertility in order to recommend fertilizers.

Our principle interest lies in this last objective. It is important from the outset to have a clear idea about the purpose of any soil study, as this will help determine sampling techniques, sample preparation methods, elements or fractions to be determined and the analytical techniques to be employed.

II Types of soil analyses

Soil analyses can be classified in various forms, such as elemental analysis or analyses of certain fractions.

Total elemental analysis determines the quantity of an element present in the soil, without reference to its "quality"; that is, its solubility or availability. The results are generally expressed in the percentages of a pure element or normal oxide per total weight after dry combustion, i.e. the weight of the soil after elimination of water and organic material. Sometimes, however, the oven dry weight is also used. It is necessary to identify the selected base to avoid confusion. The total elemental analysis is used for the purpose of soil classification or to obtain some indication of the magnitude of such production-related factors as total carbonate content and total C or N percentages. These factors, however, are seldom directly related to production, and thus the value of this technique as a fertility indicator is limited.

On the other hand, fraction analysis is generally used for fertility purposes, as well as for fertilizer recommendation, evaluation or management, and sometimes, for soil classification.

The most commonly used fractions for soil analysis are the soluble, exchangeable, extractable, retained, and mineralized fractions.

The information on soluble anions and cations is mainly used in studies of management practices, diagnosis and reclamation of salt affected soils and, less frequently, in diagnosing the soil fertility status.

The exchangeable, extractable, retained and mineralized fractions, are mainly used in soil fertility studies, though the former is also important for soil classification, management, and for reclamation of salt-affected soils.

The present paper discusses mainly the use of soil analysis as diagnostic instrument for soil fertility and fertilizer recommendations.

III The need for preliminary information

The use of soil analysis for diagnosing fertility requires prior information on the type of chemical method to be employed and the quantitative relations existing between soil analyses results and estimates of the production or response to fertilizer application. This information is obtained through correlation and calibration studies.

In general, methods selection takes place under controlled conditions. It can also be done in the field, but with less precision. In contrast, calibration is possible only in the field. It is a long process of improving preliminary inferences. Calibration as used in this paper, serves to determine the class or status of the soil fertility. The recommendation of a fertilizer dosage, although based on soil analysis results, is an economic decision and thus a separate process from calibration. It can vary in relation to input and product costs, while the fertility class of the soil remains the same. However, there are models with which one can predict yield based on soil analysis value (Coldwell, 1978).

As indicated, exchangeable and extractable fractions are the most commonly used ones. Occasionally, the total nutrient content is used. The extractable fraction, when quantitatively related with a production parameter, is called "available" or, inappropriately, "adsorbable". This last term has to be reserved exclusively for those cases in which the quantities of a nutrient that is extracted from a certain solution directly correspond to quantities or percentage of the same nutrient within a plant.

Two concepts are used when discussing soil fertility status. The first is the "sufficiency level of nutrient", which refers to the concentration of any nutrient in the soil, determined by a given method, that corresponds to a maximum physiological yield of a crop. Using this maximum-yield related concentration, several availability classes are established whose nutrient limits correspond to arbitrarily determined yield percentages. The second concept is based on the assumption that an optimal relationship between exchangeable soil bases capable of generating maximum production exists. This idea has recently been challenged, calling in question the diagnostic criterium of soil fertility and fertilizer recommendation.

Correlation and calibration studies are the back bone of any attempt at establishing routine soil analysis for diagnosing soil fertility. Extrapolating this type of information from one to another implies a serious error risk confusing and discrediting the technique.

Correlation and calibration will not be discussed in this paper.

IV Soil analysis problems

Chemical analysis for diagnosing soil fertility status consists of four generally recognized steps: sampling, preparation and analysis, interpretation of results, and making a recommendation.

For convenience, laboratory analyzed soil samples are usually dried, ground, sieved and stored. These practices can lead to undesirable changes in the sample, a fact the analist should be aware of.

The reliabilty of an analysis is based on a detailed knowledge of the proper procedure for each step and on an understanding of how certain factors can affect the results.

V Sampling

To diagnose the fertility status of any production unit by means of chemical analyses, it is necessary to obtain one or more representative samples, since processing the total soil volume is impossible. Sampling is a special process and differs from analysis steps.

To better understand this practice, it is necessary to remember some fundamental aspects. First, soil is a heterogeneous body in all directions. Second, the purpose of sampling is to obtain information on the average value of chemical and physical characteristics important for plant nutrition. Third, the size of the production unit to be sampled is not constant, but depends on how one does the sampling as well as edaphological, physiological and agronomical conditions.

Composite samples - It is well-known that the roots occupy a certain volume of soil, the magnitude of which depends on the production unit and root system depth. This can be approximately determined for a given crop.

The production unit's soil volume is composed of an infinite number of little units forming a population. According to statistical theory, it is possible to make an inference about certain characteristics of these populations by the way of extraction and analysis of a given number of samples. The more samples, the more accurate the estimates. From a practical and economical point of view, however, it is not convenient to increase this number indiscriminately. It is possible to define a desired level of precision and take an according number of samples.

There are two ways to estimate the average for a given production unit characteristic. The first is to carry out individual analyses of each of the collected samples and afterwards calculate an arithmetical average from these results. This way, however, takes a lot of time and resources. Thus, a composite sample is usually made by mixing individual samples together. The result from the composite samples should theoretically be equal to the aritmethical average calculated from the individual samples. The composite sample technique is time and cost efficient, but does not allow one to obtain measures of the spread of the data. However, this is not very important when soil fertility status is diagnosed for production purposes.

All subsamples have to be proportionally represented in the composite samples; i.e., the volume of each of the subsamples has to be equal. This is generally not taken into account during composition, which results in composite samples of doubtful quality. The use of special sampling tools (tubular augers for soil fertility) gives equal portions of soil from each sampling point in the composite.

Number of subsamples - An important aspect is the number of subsamples in the composite sample. Present recommendations place the number between 15 and 40, depending on the size and heterogeneity of the production unit. However, the heterogeneity of a little parcel and that of a large unit vary little. Therefore, the number of single samples to be collected has to be independent of the population size. Hause (1973) calculated that the maximum practical precision is achieved with 40 subsamples. His study showed that if one considers as 100% the variance that is obtained with a minimum number of samples and if the observed variances for an increasing number of subsamples are expressed as a percentage of this maximum, one can assume these variances to be a function of the inverse of the square root of n, in which n is the number of subsamples (see Fig. 1). For 15 subsamples the error is 26% and for 40 the error is 15.8%. Any increase in the number of subsamples will only slightly reduce the error.

Forty subsamples per composite sample is the recommended number when one wants to make a calibration or correlation. For diagnostic work, the number of subsamples can be reduced to 15 to 25, as a litte increase in variability will not cause a change in the soil fertility class. However, this number of subsamples is greater than that usually collected in rural soil fertility studies. One would not exaggerate in saying that the majority of samples processed in fertility laboratories are not really representative.

The danger with increasing the number of subsamples is an homogenization which translates into an increase in confidence limits. Thus it is recommended that the composite sample remains as small as possible.

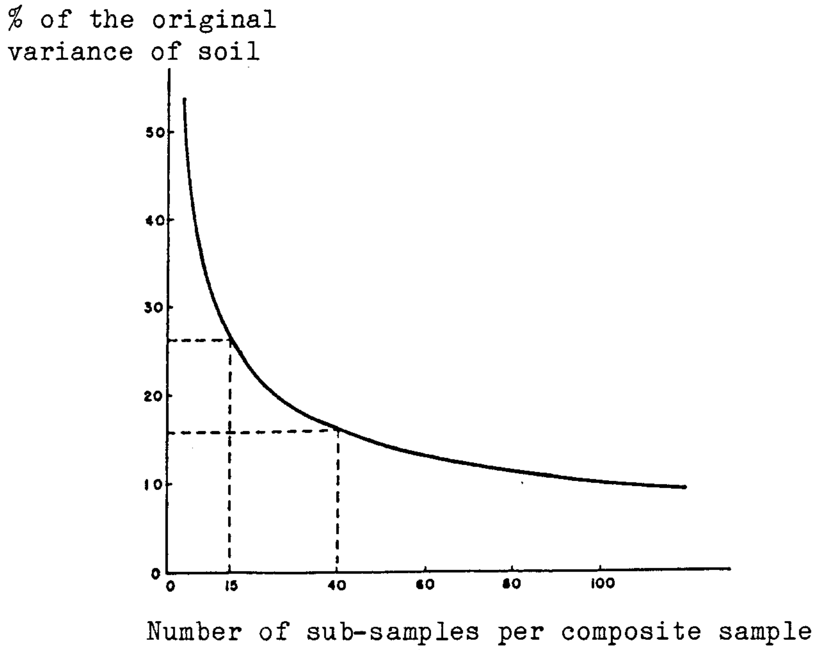

Figure 1. Relation between the number of sub-samples per composite sample and the percentage of the original variance of the soil.

Sampling depth - Sample depth is determined by the depth of the roots of a given crop. In general, maximum root activity for the annual grain crops occurs in the ploughing layer and, for most forage crops, this is concentrated in the upper 7 cm of the profile. The arable layer varies with the type of cultivation tool, a fact that should be taken into consideration in calibration programmes. Later soil samples taken for fertility diagnosis should rigorously observe the depth used in calibration.

Recently, use of greater sampling depth (up to 150 cm) has become popular for determining N-NO3 accumulation. This index correlates well with nitrogen fertilizer requirements for some crops. The main drawback is the use of a special, very expensive sampling tool. Poorer farmers need to look for other deep sampling systems, since this one is beyond the means of most.

Soil analyses for diagnosing nutrient status have not been quite successful in the case of such permanent crops as fruit trees, vineyards and forests. No recommended sample depth has been determined for them yet. It is advised to obtain series of samples of 30 cm increasing up to the desired depth. Other methods may be used for specific objectives.

In saline soils, sampling depth will be decided by the nature of the work. As a general rule, the salt crust and the germination layer (0 to 5 cm, in the majority of cases) should be sampled separately.

Sampling method - Information on this aspect is scarce. Apparently the sampling method does not affect the results, provided it is done well. Certain precautions are important in deciding on the unit to be sampled and the subsample locations, as is well known.

We would like to emphasize, however, the need for the subsamples to be represented in equal proportions. This means that the volume of each subsample, as well as of any depth increments, must be equal. This can be achieved by using some type of cilindrical tubes, although in cases like those of stony and sandy soils, such a method will not work. For these situations, it is necessary to look for suitable solutions to assure sample quality, and specially, that each sample be representative.

The following factors have to be considered in detail to improve the accuracy and precision of soil samples:

a) Variations in the concentration of chemical components may increase as the soil type changes. The color of the soil, the texture, and the topographical position show such changes. The changes are kept to a minimum if all the different soil types are sampled separately.
b) Differences in land use are a source of variation and, therefore, special sampling is necessary.
c) Sampling along old borders, electrical lines, roads, drains, canals, etc. has to be avoided. It is presumed that these soils are subject to removal and contamination.
d) When sampling grasslands, one should recall that these are generally fertilized with broadcast phosphate. Consequently the phosphate will certainly be concentrated in the first 2 to 3 cm of depth, as this element is immobile in the soil.
e) Tillage methods can affect the optimal depth of sampling. Walker et al. (1970) compared the influence of various treatments of tillage on the fertility "pattern" of a soil as indicated by the chemical analyses. Within a depth of 0-9 inches, the chemical analysis values were affected by the tillage systems (Table 1).

Similar results were found by Martinez (1979) when studying the effects of sampling in three positions: top, side, and bottom of furrows made for maize cultivation. The results for available P are presented in Table 2. The effects of the tillage and the way fertilizer is applied on the values of soil analysis require major attention if one wants to obtain representative soil samples of cultivated parcels. Further recommendations:

f) Locations near liquid or solid droppings should be avoided as sampling sites.
g) Sites where animals gather during the night, as well as former yards, should be disregarded.
h) Sampling close to canals, mole or rabbit holes, etc. is not allowed.

Table 1 - Effect of tillage treatment on average value of soil analysis of pH, P, and K in three depths (Walker et al., 1970)

	Depth of soil in inches								
	0-3			3-6			6-9		
Tillage system	pH	P	K	pH	P	K	pH	P	K
disc ploughing, cultivating and harrowing, sowing	5.7	58	340	5.6	59	298	5.4	43	277
disc ploughing, chisel ploughing, cultivating, sowing	6.1	104	487	5.5	52	262	5.2	38	246
disc ploughing, disc ploughing and harrowing, sowing in prepared furrow	5.9	60	332	5.3	39	218	5.1	31	201
rotary ploughing (twice), sowing	6.0	70	366	5.7	50	254	5.3	30	210
chopping of stalks, sowing in prepared furrows	6.0	72	425	5.3	38	216	5.1	30	204
Least Significant Difference	-	19	73	-	-	37	-	-	40

Table 2 - Effects of sample location in values of P Bray-1 in terrain cultivated with maize in furrows (Martinez, 1979)

Application1)	P Bray-1		
	Top	Side	Bottom
	ppm		
dibbled	10	8	4
broadcast	16	13	6
banding	25	12	6

1) 40 kg P_2O_5/ha as pure superphosphate

Time of sampling - In some cases, the time of year of sampling is important (Hun, 1971). The determination of available nitrate and of the soluble components in general is more time-sensitive than of phosphate, the availability of which depends largely on the capacity factor, except in volcanic soils (Table 3). Soil pH is generally different for dry and wet seasons. Differences have also been observed between the potassium concentration during autumn and that of spring, after the mineralisation of maize crop residues.

Table 3 - Seasonal variation of some nutrients in the soil (0-20 cm) in a permanent grassland (Hun, 1971)

	Element			
Month	P Extractable	fixed Phosphate	Al Extractable	K Exchangeable
	ppm	Ton P205/ha	ppm	meq/100g
December	2.1	11.3	220	0.07
January	5.3	11.0	320	0.07
February	7.7	11.0	420	0.24
March	9.3	9.7	400	0.23
April	14.0	9.7	560	0.20
May	7.8	11.5	420	0.23
June	14.8	8.6	330	0.20
July	8.9	9.2	390	0.20
August	5.9	9.5	380	0.20
September	4.6	11.0	460	0.19

1) Bray & Kurtz Nr. 2
2) Demolon
3) Morgan
4) CH_3COONH_4 pH 7 1N

VI Preparation and storage

Obtaining precise values has been one of the objectives of chemical analysis of soil. Techniques have been continuously developed, adapted and improved to fulfill this aim. However, little emphasis has been put on the handling of the sample and the drying conditions during the pre-analysis preparation phase.

Effects of drying - Wet soil is a very delicately balanced system that can be considered as a steady non-equilibrium state (Bartlett and James, 1980). Air drying causes mostly instantaneous changes which tend toward a general equilibrium, but make portions of the soil highly unstable or reactive (high entropy). Many of these are apparently associated with increased surface acidity (Bartlett and James, 1980).

Mortland and Roman (1968) attributed this phenomenon to the fact that as the clay system dries, the cations present polarize the remaining water molecules more intensely until they become more acidic than free water. As the outer sphere of water molecules is lost, the polarizing forces concentrate on the interior sphere, increasing hydrolysis and thus the ability to produce protons. The released protons could be transferred to organic components linked with the clay, which would permit an increase of its water solubility (Bartlett and James, 1980).

Table 4 presents the results of some chemical assays of spodic horizons of a soil given two treatments mentioned in Bartlett and James' work (1980): three consecutive dryings, and keeping the soil moist during the whole experiment. Tables 5 and 6 present the effect of oven and air drying on a moist sample, and the relationship between drying the sample and phosphorus and iron content in Andosols (Schalcha et al., 1965). Bartlett and James (1980) indicate that the most apparent effect to the naked-eye is an increase of the yellow or the yellowish-brown colour in extracts of samples dried three times caused by increased absorbance at 345 nm. This is in turn due to dissolved organic material (Table 4). According to Raveh and Avnimelech (1978) the increased solubility of organic material can be partly attributed to the destruction of hydrogen-bonds in the organic structure and the exposure of new organic material caused by greater acidity. This also responds in part to the disruption of microorganic cells during drying, caused by a greater surface tension in water deposited on the surface of molecules and cell structures.

Table 5 shows that both air and oven drying reduces pH as well as CEC values in volcanic soils.

Oven drying (40°C) three consecutive times causes an increase of the NH_4AcO pH 4.8 concentrations of extractable Al, Fe, and Mn in comparison with samples that were kept moist (Table 4). The increase of solubility and exchangeability of Mn with drying is a well known effect (Fijimoto and Sherman, 1945; Nelson, 1977), and it is probably due to the reduction of this element caused by the partial oxidation of organic material.

In wetland soils, however, a decrease in the Mn extractability accompanies drying (Hesse, 1971).

Schalscha et al. (1965) reported the opposite behaviour in Fe extractability for originally moist and subsequently air- or oven-dried Andosols; that is, diminished on drying while the chelated Fe increased (Table 3). Apparently this effect is due to the nature of the elemental fractions extracted, which are directly affected by drying. The previous hypothesis seems to confirm the results of P extractions presented by Schalscha et al. (1965) (Table 6). In fact, the acid extractants Bray-1 and Bray-2 solubilize lesser quantities of P in dry soils than in wet soils, while the alkaline extractant of Olsen has the opposite effect. This may be caused by the increased fragility of the organic phosphorus fraction brought on by drying.

Table 4 - Effect of drying three consecutive times and keeping wet of soil sample of a spodic horizon (B2ir) treated with 0, 5, 10 and 15 meq $CaCO_3$/10g on some characteristics (Bartlett and James, 1980)

Ajusted	Al	Fe	Mn	P	Absorbance to 345 mm$^{1)}$	
To pH	AcONH4	pH 4.8		in solution	H20	AcONH4
	ppm					
				Wet soil		
4.3	245	9	2.5	10.5	0	0.3
5.9	120	5	0.5	9.8	0	0.4
6.7	110	4	1.0	5.9	0.06	0.8
7.0	130	5	1.4	4.0	0.09	0.9
				Dry soil		
4.5	400	16	15.8	3.5	0.31	1.2
5.9	240	9	7.5	3.6	0.29	1.3
6.7	210	7	4.6	2.9	0.42	1.6
7.1	210	8	4.0	2.3	0.45	1.7

1) The intensity of the colour of the extract is indicated by the absorbance

Table 5 - Influence of method of drying on some chemical properties of volcanic ash soils (Schalcha et al., 1965)

	Soil and Horizon					
Treatment^1	Frutilar		Sta. Barbara		Pfo. Octay	
	A	B	A	B	A	B
			pH			
Wet	5.3	5.1	5.7	6.4	5.8	6.2
Air dried	5.3	5.0	5.4	6.0	5.7	5.8
Oven dry	4.8	4.8	5.0	5.3	5.3	5.5
			CEC meq/100g			
Wet	28	22	22	20	22	10
Air dried	22	22	20	12	16	10
Oven dry	18	18	14	10	12	8

1) Humid: with a moisture content equivalent to field capacity; Air dried: during 10 days at room temperature; oven-dry: during 12 hours at 105°C

Table 6 - Influence of drying method and determination procedure on extractable phosphorus and iron in volcanic ash soils (Schalscha et al., 1965)

Treatment[1]	Soil and Horizon					
	Frutilar		Sta. Barbara		Pfo. Octay	
	A	B	A	B	A	B
			Fe exchangeable + acid solution			
Wet	50	122	45	50	44	59
Air dried	40	34	28	52	30	45
Oven dried	39	32	30	33	30	32
			Fe chelatable, ppm			
Wet	154	148	72	94	64	107
Air dried	182	208	168	132	106	164
Oven dried	204	192	167	198	220	256
			P Bray-1, ppm			
Wet	33	9	2	1	0	3
Air dried	11	3	0	0	0	0
Oven dried	13	5	0	1	0	0
			P Bray-2, ppm			
Wet	50	13	7	3	2	0
Air dried	24	8	2	2	1	1
Oven dried	23	13	4	1	2	2
			P Olsen, ppm			
Wet	29	7	4	0	0	0
Air dried	53	31	34	37	35	28
Oven dried	52	36	14	35	6	5

1) Wet: with a moisture content equivalent to field capacity; Air-dried: during 10 days at room temperature; Oven-dried: during 12 hours at 105°C

Recently Leggett and Argyle (1983) studied the effect of different drying conditions on Fe, Mn, Cu and Zn extractable with DTPA in neutral and alkaline soils. The results are presented in Table 7. In general it can be said that the extractability of these elements increases with drying, and that this is more noticeable with oven drying (100°C) than with the air drying (22°C). The values obtained from freeze-dried samples were similar to those from the air-dried samples. These results confirm those of Khan and Soltanpour (1978). The increase in concentration was directly related to an increased drying temperature, and was generally less pronounced for Cu and Zn. However, the soil type affected the nature of this relationship.

The way in which dehydratation takes place has its own effect, independent on that of temperature, on micronutrient concentration. This was demonstated by Leggett and Argyle (1983), who dried wet soils at room temperature under a continuous air stream for various time periods. The soils thus had varying moisture contents that went from field saturation to completely air dry. Extractable Fe increased notably in all soils as the moisture content approached air dry; Mn, Cu, Zn, increased also, but in a lesser proportion.

Table 7 - Effects of drying conditions and moisture content on Fe, Mn, Cu and Zn extractable with DTPA (Leggett and Argyle, 1983)

Drying method	Moisture %	Extractable with DTPA			
		Fe	Mn	Cu	Zn
		ppm			
		Sonsen soil, 0-30cm			
HC	12	1.0	2.3	0.3	0.6
SA	1.1	1.8	3.4	0.4	0.8
SH	0	6.7	12.2	0.6	1.3
LI	0	2.4	4.7	0.4	1.0
		Shano soil, 0-30 cm			
HC	16	2.2	1.6	0.7	0.6
SA	1.9	4.4	1.9	1.0	0.8
SH	0	14.9	7.0	1.7	1.1
LI	0	5.8	2.3	1.0	1.0
		Portneuf soil 0-30 cm			
HC	20.0	1.8	2.9	0.8	0.5
SA	3.3	6.5	4.2	1.2	0.8
SH	0	20.9	15.2	1.9	1.3
LI	0	7.8	5.8	1.2	0.9
		Portneuf soil, 38-68 cm			
HC	20.0	1.4	4.7	3.9	2.8
SA	1.4	2.5	6.1	4.8	3.6
SH	0	5.7	6.5	5.1	5.2
LI	0	2.8	5.9	4.8	3.8

1) HC = field moisture; SA = air-dried (22°C); SH = oven-dried (100°C); LI = freeze dry (-45°C)

As with chemical properties, physical ones are also effected by the drying process. Flocculation is generally faster in air dry soils than in wet ones. The latter are easier to disperse. Kubota (1972) showed that drying causes an irreversible aggregation in volcanic soils confirming observation by Schalcha et al. (1965), that drying increased the sand fraction of these soils, while decreasing the clay fraction. Thus, physical-mechanical analysis can be appreciably altered due to the common practice of drying soil prior to analysis.

In spite of these drawbacks drying by air or in a chamber at low temperatures is the only possible way to handle an adequately number of samples for routine work. Therefore, it is important that the problems generated by this practice be completely understood.

Keogh and Maples (1973) studied various procedures that permit a rapid drying of the samples that arrived at the lab with various moisture contents. The treatments were air drying at 22°C and drying under an air stream at room temperature (22°C), 30°C and 40°C. Drying time varied from 16 to 21 days. Yet, while drying at temperatures of both 22 and 30°C produced satisfactory results, the first took 6 to 21 days to produce the required dryness, depending on the type of flask in which the drying occurred and whether or not forced air was used; while the second required only 3 to 4 days independent of the sample container. Thus, drying at 30°C is better for routine work where both speed and consistency are necessary, with the added advantage of being able to use the same container in which the soil was sent to the laboratory.

The principal changes from air drying the sample can be resumed as follows:

a) An increase or decrease of the ammoniated nitrogen concentration (fixed ammonia is released and vice-versa; the soil retains environmental ammonia).

b) An increase in sulphate concentration.

c) An increase in mineralizable nitrogen.

d) Possible changes in the extractable phosphorus fraction.

e) An increase in soil pH, except in soils that contain a relatively high amount of sulphur. Inundated soils increase their pH from 4 to 6. Drying the soil results in a removal of CO_2, which alters the carbonate equilibrium, affecting the pH.

f) In inundated soils, iron and manganese concentrations decrease with air drying. These elements undergo an appreciable increase in wet soil and decrease when it is dried. In non-inundated soils manganese increases with drying.

g) An increase or decrease of exchangeable potassium. The potassium ions can be both liberated or fixed during air drying.

h) A decrease in nitrites.

i) An increase of extractable manganese in non-inundated soils.

In general, we can say that to minimize this changes, air drying should be as rapid as possible. Oven drying, on the other hand, is not recommended for samples destined for nutrient analysis. This procedure causes considerable changes in the chemical composition of soils, particularly in Andosols.

Effects of grinding - Grinding is done to break up the aggregates and facilitate the homogenization of the sample as well as increase the specific surface.

The grinding process can cause undesired changes, such as breaking up of minerals and rocks, artificially increasing the surface exposed to chemical reactions. Another problem related with this step is that of contamination which will be discussed further on.

The grinding of a representative sample of approximately 0.3 to 1.0 kg is done manually, with a crusher or wooden hammer, or mechanically by means of rotating mill, jaw crusher or Wisconsin type mill. The metallic jawed and Wisconsin type mills, although designed specifically for soils, do not seem recommendable for this operation. Both crush little stones and pebbles, increasing the reaction surface of primary minerals present in the soil samples.

Treatment with metallic mills can result, furthermore, in very serious contamination. Iron for example can interfere with carbon determination by the Walkley and Black procedure and similar methods.

The ground soil is passed through a 2 mm sieve (approx. 10 mesh) for the majority of analyses aimed at soil fertility diagnosis. Any material that does not pass through should be removed. At the end of the operation, only stones and macroscopic organic residues should be left on the sieve. If the organic residues constitute an appreciable fraction of the total sample, the weight should be determined.

Of the sieved material, a sample of approx. 100 to 150 g is taken for later analysis. For certain micro-determinations, or when the analysis precision is to be improved, this material is passed through a 0.5 mm sieve. (approx. 40 mesh) when assaying for organic material, while for microanalysis and the studie of some micronutrients, a 100 mesh sieve is recommended. In the latter case the sample is ground in a mortar of agate or other appropriate means. Brons sieves produce Cu and Zn contaminations and should be avoided. For micronutrient analysis stainless steel sieves are best.

The segregation of particles by size that can involuntarily occur during grinding and sieving affects the results of some tests. Table 8 shows the effect of particle size on phosphorus and potassium content as determined by the double acid method. These data were generated by the author and have not yet been published.

Sometimes the separation of soils into their basic components could mean an advantage. Tan and Troth (1981) present results in which it is demonstrated that the C and N analyses for silt and clay fractions yield higher values than the analyses in the total fraction of less than 2 mm. This is particularly true for soils with a high organic material content such as Entisols and Spodosols (Table 9).

Effects of storage - The changes that occur in the soil depend not only on the method and temperature of drying but also on the duration of storage after drying (Bartlett and James, 1980). The earliest information on the effect of storage on soil refers to microbiological changes in moist samples (Hesse, 1971). Air drying moves the soil toward an equilibrium state and the water content continues to change during storage (Table 10). The results show that for certain determinations, the samples would be better preserved at a moisture content near field capacity, and at room temperature when air-dried. For longer periods it would seem preferable to maintain moist soil at 4°C.

Table 8 - Effect of size of particles on P and K extractable by double acid method (Etchevers, 1979; non published data)

Fraction	P	K
	------ppm-----	
2.0	6.5	210
0.5 -0.1	6.7	200
0.25-0.5	7.2	175
0.25	10.5	170

Table 9 - Percentage of organic carbon in total soils and in the fractions (Tan and Troth, 1981)

			Carbon				
			Clay	Silt	Sand	Total	Total soil
Order	Serie	Horizon	------------%	--------------			(<2mm)
Aridisol	Kinnear	A1	0.22	0.15	0.04	0.41	0.43
		B22	0.21	0.10	0.12	0.43	0.32
Entisol	Omega	A1	4.55	1.33	1.62	7.50	3.67
		A22	0.90	0.10	0.11	1.11	0.40
Spodosol	Onaway	A1	1.17	1.22	1.75	4.14	2.64
		A2	0.57	0.38	0.77	1.12	0.91
Ultisol	Appling	Ap	0.36	0.23	0.34	0.93	0.90
		B21t	0.17	0.1	0.05	0.23	0.25

Table 10 - Variation on concentration of Mn extractable with NH_4AcO pH 4.8 in an Aquic-Udorthent stored in three ways (Bartlett and James, 1980)

Weeks	Storage Air dry	Freeze dry	Moist at 20°C
1	14	7	6
2	19	10	6
3	22	11	5
5	26	15	6
9	26	17	8
16	38	17	8

Leggett and Argyle (1983) observed that the concentration of extractable Mn and Fe increased during storage. In general concentrations were higher in samples dried at high temperatures, in particular Mn. In contrast, Cu and Zn showed almost no variation.

The effect of storage duration is rarely considered in the results of soil analyses. The data presented here indicate that it is necessary to study this in greater detail to improve interpretation of results and look for storage methods that limit quantitatively important changes.

VII Analyses

Numerous lab operations which are part of the routine analysis can effect the result. It is supposed that these effects are greater in fractions analyses than in the total analyses, particularly those fractions extracted with acid, basic, alkaline or salt solutions. Standardizing these operations is an important step improving the reproducibility and quality of the results.

In the following we will discuss some factors that can constitute a source of error in soil analyses.

Effect of the method - The method for determining the total content of a sample should have little or no influence on the final results. This, however, is not the case with extractable fractions, where the character of the extracting solution and the operation necessary to dissolve an element or the compound that contains it indeed affect the results.

As an example, Table 11 presents the effect of the method for extracting available phosphates and determining organic carbon by wet oxidation on the results.

Table 11 - Effect of the extraction method of available phosphate and of determination of organic carbon on the results

Determination	Method 1	2	3
P, ppm	11	24	53
Organic carbon, %	6.3	9.9	11.0

1) The P figures were published by Schalcha et al. (1965) and that of organic carbon by Etchevers and Etchevers (1981)

2) Methods 1, 2 and 3 in case of P correspond to Bray-1, Bray-2 and Olsen, and in case of organic carbon to Vettori, Walkley and Black, and Ried-Copeland

The difference between available phosphate values depends on the pH of the extracting solutions and the shaking time. So, the Bray-2 (Method 2) extractant has a more acid pH than Bray-1 (Method 1), and the time of shaking is 40 sec. compared to 1 min. for the Bray-1, but the qualitative composition of the extraction solution is the same. The first method extracted more available phosphorus than the second, but did less than Method 3 (Olsen). The selection of the best extractant depends on soil type and the relationship between analytical values and the phosphorus absorbed by the growing plants.

As for organic carbon, all methods correspond to a wet digestion with a mixture of $K_2Cr_2O_7$ and H_2SO_4. The difference is based on the fact that in the first case (Method 1) external heating was used and in the other two, the heat was used from the dilution of H_2SO_4 to oxidize the organic material. In Method 1, organic carbon values were less for one of two reasons: excessive heat, causing the decomposition of $K_2Cr_2O_7$ added; or lack of heat, meaning that oxidation of the organic material available to this process is incomplete.

The analytical method used is extraordinarily important, and results vary according from one to another. Therefore, it is necessary to know the nature of the procedures before making a valid interpretation of chemical soil analysis.

Effect of solution-soil ratio - Dissolving a determined fraction of a nutrient requires extraction with a solution. The ratio of the solution-soil extraction is empirically determined from a relationship established among values of various soil solution ratios and the estimator of plant absorption for the elements in question. This may vary according to circumstances, but it must not be modified unless experimental evidence permits doing so.

Another situation has recently turned up in soil analysis. Most published solution-soil ratios are determined using soil weight. Lately, laboratories have introduced volumetrical soil measures to speed up procedures and save time. Since soils have different apparent densities, it is possible to generate slight deviations from the ideal ratios as the soil in a given volume can weigh less or more than the numerical values.

In Table 12 data are presented that demonstrate this effect and the major deviations of the soil-solution ratio.

Table 12 - Effect of the soil-solution ratio and results of extractable phosphorus following the Mehlich-1 method (Etchevers and Etchevers, 1980)

	solution-soil ratio					
	6.7	8.7	10	11.8	20	LSD
Soil	P,ppm					(P<0.05)
1	6.0	7.2	7.5	-	8.9	0.2
2	6.3	7.7	10.3	11.0	13.3	0.3

In general, as the ratio solution-soil increases, the quantity of extracted phosphorus also increases. This value would seem of no importance in the case of small deviations, due to variations in apparent density, although in the experiment all were significantly different. However, major modifications can give results that are totally inadequate for the interpretation.

Effect of shaking time and type - To get an ion or compound into solution, it is necessary to shake it with an extracting solution. The shaking time is determined empirically following the indicated lines. Rarely, however, is the type of shaking indicated. Table 13 gives data on the effect of these two variables on the quantity of extractable phosphorus according to the Mehlich-1 procedure.

Results suggests that the longer the shaking time, the greater the quantity of phosphorus that went into solution, when magnetic or side-to-side shaking was used. In the case of circular shaking, the differences were not very pronounced. This is most likely due to the vigor of this operation. There are reports in the literature indicating that in side-to-side shaking more phosphorus is extracted when the number of oscillations per minute is increased.

The data given are an example of the effect that these analytical variables can have on the results and of the need to standardize the type of shaking and velocity. It is possible that, in the case of rapidly dissolved ions like nitrates, sulphates, chlorites, these effects are not important.

Effect of size and position of flasks - Not only the type of shaking but also the position of the flasks in the reciprocating shakers effect the results. Table 14 shows extractable phosphorus results using the Mehlich-1 procedure.

Table 13 - Effect of time and type of shaking on phosphorus extractable with Mehlich-1 method (Etchevers and Etchevers, 1980)

	Shaking time (mins.)				LSD
Shaking	1	5	10	30	($P<0.05$)
Reciprocate	6.3	10.3	11.9	15.0	1.4
Magnetic	10.7	11.9	13.1	13.1	0.8
Circular	12.3	13.8	15.4	12.7	0.7

Table 14 - Effect of size of Erlenmeyer flask and position in the reciprocating shaker on phosphorus extractable with Mehlich-1 (Etchevers and Etchevers, 1980)

	Size and Position				
	125 V	125 H	250 V	250 H	LSD
Soil	ppm P				($P<0.05$)
1	5.9	11.1	11.5	11.6	0.7
2	4.9	9.1	9.5	10.0	1.3
3	6.2	8.1	8.1	9.4	0.9

1) V = vertical; H = horizontal

The data indicate that the quantity of Mehlich-1 extractable phosphate is less when the extraction is made in Erlenmeyer flasks of 125 ml placed vertically in the shaker (normal position), than that obtained with a 250 ml Erlenmeyer flask in the same normal position. The differences tend to be minimum if the first is placed horizontal in the shaker. This would indicate that to obtain comparable results, the soil particles being shaked have to move the same distance in each stroke of the shaker. This is more or less obtained when the 125 ml Erlenmeyer flask is placed in horizontal position, as its height is similar to the bottom diameter of the 250 ml Erlenmeyer flask.

This effect has also been observed when using other extractants or types of flasks (Grava, 1975).

Effect of room temperature - The room temperature influences the kinetics of the solubilization reactions. This influence would not be so important in the case of ions mostly found in soil solution or that are easily dissolved. Table 15 presents the results of experiments conducted to measure the influence of the temperature factors on extractable phosphorus.

Table 15 - Effect of room temperature on extractable phosphorus with Mehlich-1 (Etchevers and Etchevers, 1980)

	Temperature °C			LSD
Soil	11	29	50	($P<0.05$)
1	7.6	12.5	16.8	0.5
2	5.4	5.6	3.3	0.7

The effect of temperature on the quantity of phosphorus that goes to soluble form depends on how the reaction rates of dissolving and precipitation are modified. In the case of soil 1, the reaction rate of the first was greater than of the second with increasing temperature. Therefore, phosphorus in solution increased. In contrast, in soil 2 higher temperatures occurred and phosphorus in solution decreased.

This information cannot be applied to other methods and elements without further study, but based purely on kinetics we can say that that the situation may be similar to other ions that behave like phosphates.

Effect of contact time - After the soil has been shaken with any extracting solution, the liquid phase will be separated from the solid phase by decantation, centrifugation, or filtration. The first practice can lead to errors, as the soil will remain in contact with the solution for a long period. In Table 16, the effect of contact time is demonstrated on the quantity of phosphorus in solution.

Table 16 - Effect of contact time on extractable phosphorus with Mehlich-1 (Etchevers and Etchevers, 1980)

	Contact time, hrs.						LSD
Soil	0.25	0.50	1.0	1.4	24	48	(P<0.05)
1	6.5	6.1	6.1	5.9	2.8	1.9	0.5
2	9.3	7.9	7.2	-	5.6	-	0.9

The data show the importance of executing the separation of both phases as soon as the shaking is finished. Leaving the extractant solution in contact with the soil can lead to undesirable reactions.

VIII General conclusions

The following conclusions can be derived from the analyses presented:

1) Sampling is a crucial phase in obtaining reliable results;
2) The steps that form the preparation of a sample, that is, drying, grinding, storing, and the phase of analysis, affect the results and therefore should be standardized;
3) The interpretation of soil analysis can only be valid when they are based on previous studies of calibration;
4) Chemical soil analysis is useful as diagnostic method only when it is executed with the same analytical procedure as those that were used for calibration;
5) In the description of the calibration all the details have to be given of the chemical procedures applied, so that they can be reproduced later.

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SOIL ANALYTICAL PROCEDURES AND RECENT INTERLABORATORY CROSS-CHECKING IN ARGENTINA

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ABSTRACT

In the last few years at least three significant activities of control and evaluation of analytical data furnished by soil laboratories were carried out in Argentina.

The first one was a comparison of analytical data and fertilizer recommendations furnished by several institutional and private soil laboratories; the second one was a joint action between official and private laboratories to compare results and to evaluate the origin of variation; the third one was an institutional programme in which several laboratories of an official institution worked combined to standardize the methods for fertility diagnosis.

The first conclusion that can be drawn from these experiences is the great variability in results, including those analytical determinations that seemed relatively simple. Secondly, the use of a standard method in some cases didn't result in a decrease of the variability in analytical results while in other cases, and through a better identification of variation sources, it was possible to obtain more homogeneous results.

Some examples are discussed and some possible sources of variation in soil analytical determinations are mentioned.

I Introduction

Various circumstances have often made clear the quality problems in analytical data supplied by soil laboratories. In some countries this has lead to a control and evaluation effort of work between laboratories, and subsequently to an attempt to improve the quality through standardisation of analytical procedures (Van Reeuwijk, 1984).

Also in Argentina, various experiments have been carried out for this purpose; their organisation and execution were each time different, and so was their degree of success.

II The first control experiments

1. At different occasions, two or three laboratories worked together to compare and improve their analytical methodologies and results. An example of this is the cooperation between the laboratory of the Soil Institute of INTA in Buenos-Aires and the laboratory of the Ministry of Agriculture in the Santa-Fé Province, at the beginning of the Soil Map Programme of the Pampa-region, which started in 1968.

2. However, probably the first experiment with a greater number of participants was carried out by Panigatti et al. (1971), comparing analytical data and fertilizer recommendations given by ten laboratories from one soil sample.

The conclusions of this comparison can be summarized as follows:

a. the analytical results of the various laboratories showed a great variability;

b. the results of the same parameter were expressed in different ways;

c. the interpretation of the data and fertilizer recommendations disagreed, even for similar analytical data.

3. Some years later, as a consequence of these dramatic facts, the Chemical Committee of the Soil Science Society of Argentina undertook an evaluation of the analytical methods used in the soil laboratories. Therefore a very detailed questionnaire was prepared about the used methods, which was sent about 1980 to all laboratories in the country.
Nevertheless it appeared that the questionnaires were too long and too detailed; this had as result that only a fraction of the laboratories returned the requested information, which has not been evaluated until now. Out of this experience the lesson can be drawn that either the request of information has to be limited to certain essential points or that different steps should be made, where each step refers to some analytical methods only.

III The recent experiments

1. The work between institutes

In 1982, out of the initiative of a farmers organization, worried about the differences between the data from various sources, several instutional and private laboratories of the Pampa region began to work together to trace the origin of the variability and to solve the divergencies. (AACREA, 1982; 1983; Daniel 1983).
As first step, a synoptical comparison of the methods used by each participant was made for a limited number of soil parameters (organic C, total N, nitrates, available P, pH and electrical conductivity). At the same time, as laboratories always make internal controls and adjustments of methods, the participants exchanged their own experiences on the advantages and disadvantages of each method or modification, as well as on possible sources of variability of the analytical results.
Then, the group undertook a cooperative effort of quality control, by analyzing several soil samples with their own routine methods. Then, and for all evaluated parameters, significant differences appeared between the results of the various laboratories.
Next, and through various activities such as discussion meetings, analyzing of available information, collaborative work (comparison of results between two or three laboratories using one method), the origin of the divergencies between the analytical results was investigated. Various interpretations and conclusions can be drawn from the work done by this group:

a. PH-H_2O

Although this soil property can be considered as very simple to measure, the comparison showed differences exceeding one unit, between the laboratories for the same sample (table 1). The work carried out however has allowed to identify the following sources of variability:

- the pH of distilled water used for the suspension of the sample;
- the length of time of soil-water contact; the experiment carried out by one of the participating laboratories showed that, in the first hour of contact (and depending on the soil type), considerable fluctuations in pH can appear;
- the position of the electrode; here more than 0.5 pH unit difference was recorded whether the electrode was immerged in the clear supernatant or

in the bottom part of the suspension. However, no correlation was found between the position of the electrode and the pH, since this variation seems to depend on the type of sample: in some cases the values measured in the bottom part of the beaker are higher than those measured in the supernatant, while in other cases the opposite results are obtained.

b. Electrical conductivity

The measurement of the electrical conductivity in the saturated paste showed also significant variations. Experiments carried out by one of the laboratories showed that the contact time is here also very important, in particular in the case of saline and alkaline soils, of which the conductivity can fluctuate considerably during the first hour of contact.

c. Available P

Although all laboratories used the method Bray No 1, important differences in the results were found. However their source has not been found, since this task was complicated in the way that two of the laboratories obtained similar results with rather different procedures (grinding and sieving of the sample, time and type of extraction, volume of used aliquot, etc.).

d. Organic C

Here also marked differences were reported in the results (table 2). However, comparing the laboratories B (which used a micro type of the Walkley & Black method) and C (macro method), systematic differences were observed; this led to the explanation that one of the sources of error of laboratory B was a too small (0.1 g) and too fine ground and sieved (0.15 mm) sample; the errors were particularly clear by the low-organic and/or coarse-textured samples, probably because laboratory assistants might have had the tendency to discard the coarse sands during manual grinding of the sample. This source of error in the carbon analysis of coarse-textured soils was also mentioned by Godefroy (1977).

e. Total N

This is another soil characteristic in which significant variations were found between the results of the various laboratories. Constant differences between laboratories B and C were reported, which could have the same origin as those mentioned for organic C.

After two years , this inter-institutional control and evaluation work was stopped; although it has been short, several benefits were obtained: on one hand, it was possible to evaluate and even to identify some possible sources of variation of the analytical data, and consequently, to adjust the procedures of participating laboratories; on the other hand, resulting from the problems about quality of the analyses brought to the daylight by the work of this group, reference samples, analysed beforehand by three of the most important laboratories of the country, have been made available to the soil laboratories by the Soil Science Society of Argentina.

2. The intra-institutional experience

In 1984, and in connection with a governmental fertilizer promotion programme, the INTA laboratories located in the Pampa-region (some of whom have participated in the above mentioned experiments), convened to control and standardize some analytical methods on soil fertility.

In a first phase, the methods used by the participants were compared: for some of the parameters, the methodologies were almost similar for some of these (e.g. for organic C), while for others (e.g. for total N and nitrates) different versions were used.

In a second phase, the participants analyzed a soil sample and a solution containing phosphorus: important variations were noted for the soil sample (including the available P), while substantially homogeneous results were obtained for the phosphorus solution (table 3). This fact demonstrates that for phosphorus the variability originates mainly from the extracting procedure of the element.

Following this first data control, the methods used were discussed and some research work on the routine methods was undertaken. In this way, for instance about the extraction of available phosphorus, it was found that the horizontal shaking of the sample gave better results than vertical shaking (table 4).

At last, in a third phase, the participating laboratories twice analyzed soil samples using previously standardized methods.

This experiment, that lasted for one and a half year, resulted in a satisfactory degree of reproducibility among the majority of participants for most of the evaluated methods (organic C, total N, absorbable P, pH), and this was statistically demonstrated by a marked decrease of the coefficient of variation (table 4). On the contrary, for the analysis of soil nitrates, no succes was obtained in reducing the considerable variations.

IV Conclusions

In Argentina, and specially very recently, various experiments of control of analytical data have been carried out, as well as the evaluation and standardization of the methods used by the soil laboratories.

Through the first control of various laboratories, carried out about 1970, one became aware of important divergencies in the results. Later, in the 80's, and through the intra- and inter-institutional work, which included cooperative and collaborative work, the sources of variability were investigated, and adjustments of the methods were proposed to obtain better quality results.

This work has certainly been short and incomplete; in some cases, one has succeeded in improving the analytical results, while in other cases no success has been booked. However, from the carried out experiments, it seems possible to derive some recommendations to improve the quality of soil analysis:

- <u>pH-H_2O</u> (1:2.5): make the measure after two hours of water-soil contact; measure the pH in the agitated suspension; control the quality of distilled water, buffer solutions and electrodes.
- <u>Electrical Conductivity</u> (saturated paste): measure the conductivity after two hours of water-soil contact.
- <u>available P</u> (Bray and Kurtz No 1): extraction with horizontally placed tubes in a reciprocating shaker.
- <u>Organic C</u> (Walkley and Black): from the results obtained it seems convenient to use the macromethod, with a sample quantity related to the probable organic matter content. For instance, for the Mollisols and Alfisols of the Pampa of Argentina, for the A horizons: 0.5-1 g of soil; B horizons: 2 g; C horizons: 3-5 g. Moreover the sample should not be ground and sieved finer than 0.5 mm.
- <u>total N</u> (Kjeldahl): it seems also convenient to use the macromethod, with 1-2 g of sample sieved to 0.5 mm.

These recommendations are made from fragmentary experiments. Therefore they are open to improvement or modification through more detailed work. Notwithstanding, they indicate to us that it would be possible to improve soil analysis through identification and normalisation of the critical points in each analytical method.

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pH (H_2O, 1:2,5)

MUE- LAB-	pH H_2O	1	2	3	4	5	6	7	8
A	—	6,2(1)	6,3(1)	6,4(1)	7,1(3)	6,5(1)	6,3(1)	6,4(2)	6,2(2)
B	5,7	6,7(2)	7,1(3)	6,9(2)	8,4(2)	6,9(2)	6,9(2)	6,4(2)	7,0(2)
C	—	6,2(1)	6,6(1)	6,6(1)	7,9(1)	6,4(1)	6,2(2)	5,8(2)	6,2(2)
D	5,1	6,3(1)	6,2(1)	6,5(1)	8,5(2)	6,2(2)	6,6(1)	5,5(3)	6,7(1)
E	4,3	5,3(3)	5,6(3)	5,5(3)	7,2(3)	5,6(3)	5,6(3)	5,1(3)	5,6(3)
F	—	6,2(1)	6,2(1)	6,5(1)	7,9(1)	6,3(2)	6,3(1)	5,8(3)	6,4(1)
G	5,3	6,4(1)	6,6(1)	6,8(1)	8,3(1)	6,4(1)	6,5(1)	5,9(1)	6,6(1)
H	—	5,6(3)	5,8(3)	5,8(3)	7,4(3)	5,8(3)	5,7(3)	5,2(3)	5,9(3)
I	—	6,8(2)	6,7(1)	6,6(1)	7,2(3)	6,6(1)	6,6(1)	6,8(3)	6,8(1)
J	—	6,4(1)	6,6(1)	6,5(1)	7,8(2)	6,5(1)	6,5(1)	6,1(1)	6,4(1)
K	5,8	6,8(2)	7,1(3)	7,0(2)	8,2(1)	6,9(2)	6,8(2)	6,4(2)	6,9(2)

L_1 = ± 0,2 unid. pH ; L_2 = ± 0,5 unid. pH
(1) = L_1 ; (2) = L_2 ; (3) = fuera de L_2

N° Det.	L_1	L_2
8	1	4
7	1	4
6	1	1
5	4	0
4	0	0
3	0	0
2	0	0
1	1	0
0	3	2

Table 1: pH of soil samples and distilled water; inter-institutional cooperative experiment (Daniel, 1983).

C Org. Total

MUE· LAB-	1	2	3	4	5	6	7	8
A	1,48(1)	0,94(1)	1,15(1)	1,54(2)	2,24(1)	1,85(1)	1,49(1)	1,53(2)
B	1,49(1)	1,68(3)	2,02(3)	2,02(3)	2,14(1)	1,71(2)	1,47(1)	1,62(3)
C	1,42(1)	0,92(1)	1,17(1)	1,40(1)	2,28(1)	1,72(1)	1,31(2)	1,39(1)
D	1,10(3)	0,81(3)	0,88(3)	1,20(3)	2,01(2)	1,37(3)	1,08(3)	1,06(3)
E	1,42(1)	1,01(1)	1,20(1)	1,46(1)	2,28(1)	1,80(1)	1,24(3)	1,43(1)
F	1,90(3)	0,50(3)	0,80(3)	1,60(3)	2,70(3)	1,40(3)	2,30(3)	2,70(3)
G	1,35(2)	1,20(3)	0,85(3)	1,37(1)	2,03(2)	1,63(2)	1,08(3)	1,29(2)
H	1,50(1)	1,00(1)	1,97(3)	0,52(3)	2,18(1)	1,91(2)	1,48(1)	1,53(2)
I	1,16(3)	0,97(1)	1,16(1)	0,78(3)	0,78(3)	1,16(3)	1,16(3)	0,97(3)
J	1,72(3)	1,20(3)	1,31(3)	1,72(3)	2,82(3)	2,33(3)	1,77(3)	1,89(3)
K	1,38(1)	0,98(1)	1,32(3)	1,45(1)	2,33(1)	1,86(1)	1,37(1)	1,41(1)

$L_1 = \pm 5\%$; $L_2 = \pm 10\%$

(1) = L_1 ; (2) = L_2 ; (3) = fuera de L_2

N° Det	L_1	L_2
8	0	2
7	3	2
6	1	1
5	0	1
4	1	1
3	1	0
2	1	1
1	1	1
0	3	2

Table 2: organic C; inter-institutional cooperative experiment (Daniel, 1983).

Unit	pH	P Bray ppm	org. C %	total N %	C/N	solution P ppm
Edaf. Agricola	5.50	42.75	1.95	0.144	11.67	4.00
Castelar	5.70	42.90	2.03	0.185	10.97	3.54
Rafaela	4.60	46.73	1.69	0.168	10.06	4.06
Bordenave	5.65	44.00	2.40	0.190	12.63	3.78
Ascasubi	6.00	47.00	2.03			3.50
Pergamino	5.60	42.80	1.45	0.169	8.58	3.63
San Pedro	5.50	50.10	2.10			3.93
C.Uruguay	5.40	21.00	1.99			3.76
M. Juarez	5.40	38.00	1.86	0.155	12.00	3.50
Parana	4.80	47.86	2.10	0.153	13.73	3.78
Balcarce	5.70	47.73	1.95			4.05
Anguil	5.43	46.93		0.170		4.10
Oliveros	-	50.00	2.07	0.163	12.70	4.00
Manfredi	5.84	32.4	1.91			3.70

Table 3: results of the analysis of a soil sample and of a phosphorous solution; intra-institutional cooperative experiment (INTA, 1984).

A - ANALYSIS OF ABSORBABLE P (in ppm of P)

Laboratory Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	37.2	45.14	33.0	33.0	37.50		26.0	33.0	37.9	34.9	33.6	34.8		
2	51.80	50.68	45.0	46.2	49.50		35.0	45.0	51.2	48.7	44.8	45.0		
3	6.60	5.94	5.0	4.6	5.42		5.0	7.0	9.8	5.8	6.8	7.4		
4	45.20	50.68	42.0	35.0	45.07		31.0	39.0	47.0	43.0	42.0	42.0		
5	68.0	83.15	61.0	-	63.41		47.0	63.0	69.9	66.0	67.8	68.8		
6	25.84	31.28	26.0	27.3	27.10		22.0	28.0	33.4	27.1	28.8	28.8		
7	41.60	47.52	41.0	42.0	42.00		34.0	44.0	49.9	41.8	43.8	47.6		
8	72.0	68.90	65.0	58.8	72.37		49.0	65.0	90.4	69.0	66.8	67.0		

B - Computed data of 11 laboratories (ppm)

Sample No	$\bar{x}$ (ppm)	(n) (ppm)	CV (%)
1	35.094	4.443	12.66
2	46.625	4.505	9.66
3	6.305	1.404	22.27
4	41.995	5.222	12.43
5	65.806	8.519	12.95
6	27.783	2.819	10.14
7	43.202	4.054	9.38
8	67.661	9.551	14.12

C- Computed data of 8 laboratories (ppm) which agitated the soil/extractant horizontally

Sample No	$\bar{x}$ (ppm)	(n) (ppm)	CV (%)
1	34.625	1.731	5.00
2	47.00	2.491	5.30
3	6.077	0.952	15.67
4	41.658	3.117	7.48
5	65.43	2.746	4.22
6	27.367	1.052	3.84
7	42.975	2.006	4.67
8(*)	66.996	4.079	6.09

(*) Excluding lab. no. 4, which had problems especially with this sample, CV lower than 4.16%.

Table 4: Intra-institutional experiment; results of the analysis of absorbable P. A and B: cooperative experiment (each laboratory with his own method). C: collaborative experiment (same system of agitating the soil horizontally) (INTA, 1984).

THE INTERNATIONAL PLANT SAMPLE EXCHANGE *)

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I Introduction

Many laboratories are involved in plant tissue analysis, and the question of how well laboratories agree on the results is often asked. To answer this question, a collaborative study has to be conducted to evaluate the interlaboratory variability. Such a study has been conducted by our university since 1956 and at the time being about 190 laboratories from 54 countries all over the world are participating. In the following evaluation the data from the period 1981-1985 are used. All data were obtained by the particular methodology routinely used by each laboratory. The parameters involved are: Al, B, Ca, Cd, Cl, Co, Cr, Mn, Fe, Cu, Mg, K, Mo, N, Na, Ni, NO_3, P, Pb, S, Se, SO_4, Zn.

II Calculations

After outlying values had been rejected the average value and standard deviation were calculated for each parameter and each sample. From these the coefficients of variation (c.v.) were calculated:

c.v. = (standard deviation / average) * 100%

These coefficients of variation were then plotted as a function of corresponding average content of the parameters in the different plant tissues.
The general pattern in the plots is, as expected a constant c.v. over a broad range of concentrations, strongly increasing in the lower concentration range.
From the plots two values can be read:
- the level of the 'constant' c.v.
- the value of the average, where c.v. strongly increases.

The 'constant' c.v. range can be considered as inherent to interlaboratory variation in cases where no analytical-technical difficulties are present. The value where c.v. strongly increases, can be considered the 'lowest measurable content' of the parameter.

III Results

For the following parameters the constant interlaboratory variability amounts to about 10%:

c.v. (%)	parameters
5 - 10	Cl, K, Mg, N(total), P
10	Ca, Cu, Mn, Nitrate, Zn
10 - 15	B, Fe, Na

For the other parameters studied no such clear-cut trend was observed, which means that the analytical difficulties are such that interlaboratory comparison is not feasible.

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*) This contribution is a short version of a full paper in the Netherlands Journal of Agricultural Science (Houba e.a., 1986). Copies are available from the authors of from the Labex Secretariat.

Comparison of the lowest measurable amount with the 'normal' content range, as reported by different authors, shows the following. The precision found for N, P, K, Ca, Cl, Zn and nitrate was high enough (c.v.<20%) to yield reasonable comparable content values. Comparison of analytical results for B, Cu, Fe, Cd, Mn and Na may be difficult, since about 20% c.v. was reached already at the levels usually present in plant material. The analytical results for Al, Co, Cr, Mo, Ni, Pb, S, Se and sulphate varied considerably, irrespective of the content level, which means that comparable results are very hard to produce with these components.

Generally speaking, the present results reveal that for a great number of parameters further analytical chemical investigations and optimisation of the methods used are urgently needed.

Reference

Houba, V.J.G., I. Novozamsky and J.J. van der Lee, 1986. Inorganic chemical analysis of plant tissue: possibilities and limitations. Netherlands Journal of Agricultural Science 34:449-456.

ON THE WAY TO IMPROVE CEC ANALYSIS IN SOIL: A NEW COMPREHENSIVE SINGLE STEP PROCEDURE WITH LiEDTA *)

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I Introduction

Cation exchange capacity and contents of exchangeable cations are among the most important soil chemical properties. It is therefore remarkable that quantitative estimation of cation exchange characteristics is generally very laborious and that no satisfactory method exists for calcareous and gypsiferous soils. Conventional methods for determining cation exchange capacity and exchangeable cations involve saturation of a soil adsorption complex with a selected cation, washing out excess salt and assaying the amount of that cation after exchanging it with a different cation. The extractions are normally done by percolation or centrifugation.
These methods involve various time consuming extraction-, percolation- and washing steps that may lead to serious errors due to hydrolysis, salt retention and loss of material.

II Single step procedures

From 1975 on methods have been developed, based on the use of silverthiourea (AgTU), cobaltihexammine (CoHA) or lithium-EDTA (Li-EDTA).
These methods are similar in use and ease in needing a single extraction for CEC and exchangeable cations, but they work principally different:

- using a replacing complex-ion with high affinity of the soil complex:

AgTU : $Ag(SC(NH_2)_2)_n^+$

CoHA : $Co(NH_3)_6^{3+}$

- using the high affinity of a soluble ligand for multivalent exchanged cations:

LiEDTA : $H.EDTA^{3-}$

III The LiEDTA and LiBaEDTA methods

1. Principle

By incubation of a soil with excess LiEDTA, both Li and EDTA have a function: Li exchanges adsorbed cations and EDTA chelates the replaced Ca and Mg, keeping the activity of these cations in the solution at a very low level. Moreover Ba in LiBaEDTA has a third function: added to gypsiferous soils LiBaEDTA precipitates all sulphates as $BaSO_4$ and chelates Ca^{2+} with EDTA.

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*) This contribution is a short version of a full paper in 'Communications in Soil Science and Plant Analysis' (Begheyn, 1987). Copies are available from the author or the Labex secretariat.

2. Advantages of Li

Li is rarely used as replacing cation in CEC analysis because of its relatively low affinity for soil colloids. When added as LiEDTA or LiBaEDTA however, Li adsorption is compulsory because Ca and Mg are desorbed as a result of the chelation by EDTA. Advantages of the use of Li are:

a) normally it is not present in soils

b) it is not subject to hydrolysis

c) it can easily and accurately be determined by flame emission photometry

d) fixation by clay minerals is low, compared to other less strongly hydrated cations as NH_4, K, Rb and Cs.

3. Stability constants

3.1 Chelation of metalions

Chelation by EDTA is represented by the equation:

$$M + Y = MY$$

in which M is a metal ion and Y is the ligand. This equilibrium is governed by the constant K.

$$K = (M).(Y) / (MY)$$

In practice EDTA (Y^{4-}) also reacts with water to form HY^{3-} or even H_2Y^{2-} and H_3Y^- (protolysis) which reactions are pH dependent. This hampers the chelation of the metal, and apparently influences the equilibrium constant. In a H_2O environment the metal-EDTA equilibrium is defined by this apparent stability constant, Ka, which is pH dependent. Table 1 shows the equilibrium constant K and the apparent stability constants Ka for a number of cations.
The higher these values, the more stable are the complexes. From this table it appears that of the cations that are common in soils, only Ca, Mg and Al form stable complexes with EDTA.

3.2 Dissolution of gypsum.

In the exchange process with LiBaEDTA solution gypsum dissolves while sulfates are removed by precipitation as $BaSO_4$. A mineral will dissove in EDTA if the product of the apparent stability constant (Ka) of the metal-EDTA (MY) complex and of the solubility product (Ksp) of a salt (MX) exceeds unity.
As log Ksp($CaSO_4$) = -4.6 and log Ka(CaEDTA) = 7.2, $CaSO_4$ dissolves.
As log Ksp($BaSO_4$) = -10.0 and log Ka(BaEDTA) = 4.4, $BaSO_4$ precipitates.

$$LiBaEDTA(aq) + CaSO_4(s) \longrightarrow LiCaEDTA(aq) + BaSO_4(s)$$

Precipitation of $BaSO_4$ at pH 7 is enhanced because Ka(BaEDTA) is much smaller than Ka(CaEDTA), so Ca is preferentially chelated with EDTA.
Other relatively soluble minerals such as calcite, dolomite, and magnesite also dissolve to an appreciable extent in EDTA. Silicates, including most clay minerals, however are hardly affected.

Table 1: Equilibrium Constants (K) and Apparent Stability Constants (Ka) of some metal-EDTA complexes (Begheyn, 1987).

metal	log K	log Ka pH 6	log Ka pH 7	log Ka pH 8
Li	2.8			0.5
Na	1.7			
K	0.96			
Ca	10.6	5.9	7.2	8.3
Mg	8.7	4.0	5.3	6.4
Ba	7.8	3.1	4.4	5.5
Al	15.5	10.8	12.1	13.2

Solubility products (Ksp)

	log Ksp
$CaSO_4$	- 4.6
$BaSO_4$	- 10.0

IV Outline of procedures

1. Extractants

1.1 LiEDTA (0.1 M Li, 0.03 M EDTA), pH 8.0
dissolve 9.2 g H_4EDTA and 4.2 g $LiOH.H_2O$ in 1l H_2O
1.2 LiBaEDTA (0.2 M Li, 0.05 M Ba, 0.08 M EDTA), pH 8.0
dissolve 23.38 g H_4EDTA, 15.77 g $Ba(OH)_2.8H_2O$ and 8.39 g $LiOH.H_2O$ in 1l H_2O
1.3 Na_4EDTA (0.5 M)
dissolve 146 g H_4EDTA and 80 g NaOH in 1l H_2O

2. Procedure for neutral soils (non saline) and acid soils

LiEDTA extraction: 0.25 - 2.5 g sample
10.0 ml LiEDTA
incubate 1h.
shake 15 mn.
centrifuge
Analyse in extract: Li, Na, K, Ca, Mg, pH-eq
pH of extract (pH-eq) is the equilibrium pH for the CEC.
buffer capacity: pH 6.5 - 7.5

3. Procedure for calcareous soils

LiEDTA extraction: as above except for Ca and Mg
(CEC = A mmol/g; moisture % = B)
Na_4EDTA/ethanol extraction: 1.0 g sample
1.0 ml ethanol
A ml Na_4EDTA
(1 - A - B/100) ml H_2O
incubate 1 h.
swirl every 15 min.
centrifuge
analyse in extract: Ca and Mg.

4. Procedure for gypsiferous soils

LiBaEDTA extraction: 0.25 - 2.5 g sample
10.0 ml LiBaEDTA
shake 12 h.
centrifuge
analyse in extract: Li, Na, K, pH-eq
for Ca and Mg: Na_4EDTA/ethanol extraction as above

5. Procedure for sodic soils

for neutral soils: LiEDTA extraction as above
for gypsiferous soils: LiBaEDTA extraction as above
correction of CEC and estimation of ESP:

f = (Li) / ((Li)-(Na))   (in extract)

CEC(I) is CEC as determined with extraction
CEC(II) = CEC(I) x f
Na(exch) = Na(extr) + (CEC(II) - CEC(I))

ESP = 100 x Na(exch)/CEC(II) (%)

6. Procedure for saline soils

for neutral, gypsiferous or sodic soils: extractions as above
analyse in extract: Cl, Na(exch + sol)
Na(exch) = Na(exch + sol) - Cl

V Some results

Figure 1 gives some results of the CEC with Li(Ba)EDTA and NH_4OAc methods. The samples are the Labex samples no 1 to 28. These include also saline and calcareous samples. The LiEDTA-CEC, determined in our laboratory, is plotted against the NH_4OAc-CEC, as reported in the Labex reports. When extreme values, over 300 meq/100 g, are discarded a good correlation exists. Regression of NH_4OAc-CEC (Y) on LiEDTA-CEC (X) results in:

$Y = 1.19 X + 1.81$ $r^2 = 0.933$

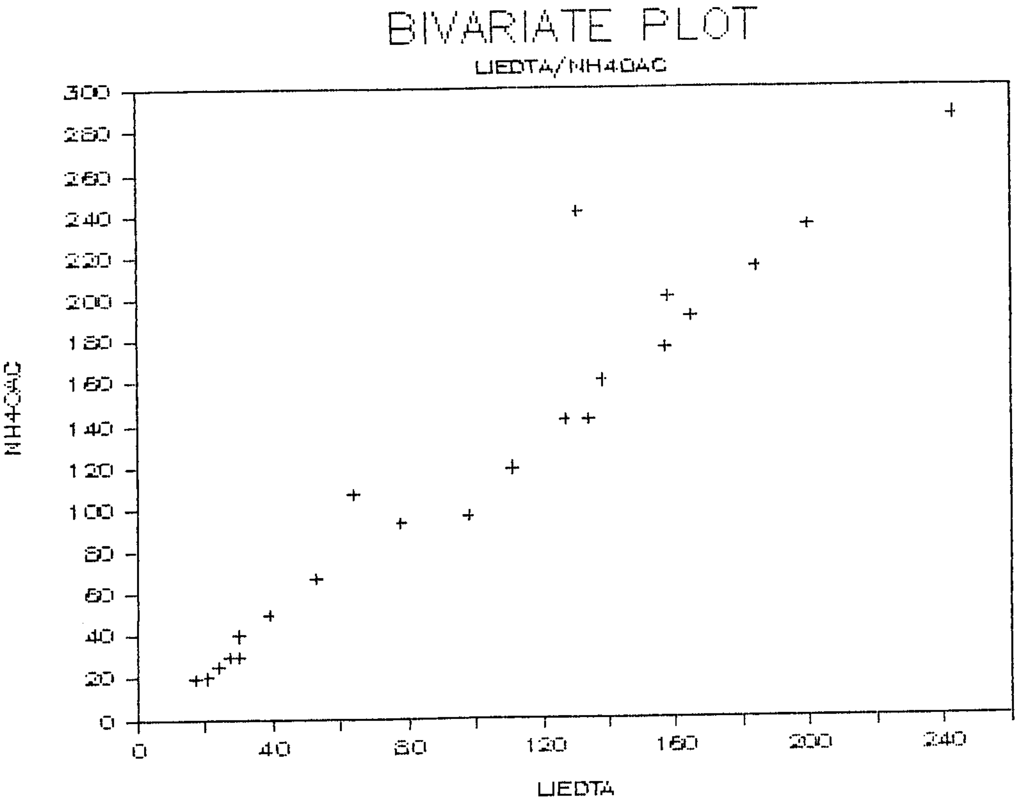

Fig. 1. Bivariate plot of CEC-LiEDTA and CEC-NH_4OAc

VI Conclusion

In conclusion, LiEDTA appears to be a suitable and very convenient extractant for analyzing CEC and exchangeable bases in non-calcareous and, together with Na_4EDTA, in calcareous soils. Use of Ba in LiBaEDTA extends the application of the LiEDTA procedure to gypsiferous soils.
The method is not laborious and is low in cost and waste. A flamephotometer is sufficient for the analysis of Li, Na, K, Ca and Mg in the abstracts. Using diluter and computer the procedure can be extremely automatized in operation and data management.
I am convinced that this will be recognized as a serious candidate for a new reference method and that it will contribute on the way to improve CEC analysis of soils.

References

Begheyn, L.Th., 1987. A rapid method to determine Cation Exchange Capacity and Exchangeable Cations in soils, including calcareous, gypsiferous, saline and sodic soils. Comm. Soil. Sc. Plant Anal. (in print).

EXTRACTION OF CATIONS FROM SOME KAOLINITIC SOILS OF THE TROPICS

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I Introduction

In previous work it was shown that AgTU (silver-thiourea) can be used for extraction of cations and for measuring CEC of various soils from temperate and tropical regions (Chhabra et al., 1975; Pleysier and Juo, 1980; Pleysier et al., 1986; van Rosmalen, 1980). Results of the AgTU method generally agree with those of the NH_4OAc method for exchangeable cations and CEC. For some soils, however, considerable differences in extracted cations between the methods occur. For example, the amount of K extracted from a variety of soils from temperate and tropical regions by a single extraction with dilute buffered or unbuffered AgTU solution ranges from about 90 to nearly 200 percent of the amount of K extracted by three extractions with neutral $\underline{N}$ NH_4OAc (Pleysier and Juo, 1980 ; Chhabra et al., 1975). This observation is surprising because the concentration of the AgTU solution is only 0.01 $\underline{N}$ and also because NH_4^+ is considered to be an efficient cation for displacing K^+.

Rather large differences between CEC by unbuffered AgTU and by neutral $\underline{N}$ NH_4OAc were observed for acid soils with high organic matter content (Chhabra et al., 1975). These differences in CEC correspond with differences in extractability of Ca and Mg by both methods.

For various kaolinitic soils a higher total titratable acidity in dilute AgTU than in $\underline{N}$ KCl extracts was observed (Pleysier and Juo, 1980).

This study was undertaken to further investigate the extractability of various cations by AgTU and by NH_4OAc and KCl solutions in some kaolinitic soils from tropical regions. The amount of K extracted by AgTU and by NH_4OAc was compared with the amount of K extracted by hot H_2SO_4. The latter is often used as an index for plant-available K in soil (Hunter and Pratt, 1957).

II Materials and Samples

Soil samples

A variety of surface and subsoil samples, including Alfisols, Ultisols, Oxisols, Entisols and Inceptisols, were used in this study. The samples came from Togo, Tanzania, Ghana, Ivory Coast, Liberia, Kenya, Brazil, Cameroon, Sierra Leone, Sao Tome and Nigeria. Some properties of the soils are given in Table 1. The samples were air-dried, ground and passed through a 2-mm sieve. Subsamples were pulverized for organic carbon analysis by dichromate oxidation method. The pH was measured in a 1:1 soil/water suspension. Clay content was measured with a hydrometer after oxidation of organic matter (with H_2O_2) and dispersion with calgon.

Clay minerals

Subsoil samples were analyzed for clay minerals. The clay minerals in the clay fraction were determined on salt-free samples brought into the Ca form. Diffraction spectra of the oriented samples, coated on glass slides, were taken with a Seifert-Scintag PAD II diffractometer before and after equilibration of the samples with a saturated ethyleneglycol atmosphere.

Extraction of cations

Potassium was extracted by three different methods. In the first method, 5 g of soil were extracted with three 30-ml portions of neutral N NH_4OAc. The filtered extracts were combined and brought up to 100 ml with the extractant. The total extraction time was about one and a half hours. Ca, Mg and Na were also measured in these extracts.

Extraction of K by the second method was done by shaking from 1 to 10 g of soil sample (depending on the CEC) with 30 ml of 0.01 N unbuffered AgTU solution. The samples were shaken in centrifuge tubes for 2 hours. K, Ca, Mg, Na and Al+H were measured in the AgTU extracts after centrifugation. The AgTU solution was prepared as described before (Chhabra et al., 1975; Pleysier and Juo, 1980).

The third method for extraction of K was done with dilute H_2SO_4 as described by Hunter and Pratt (1957). Only subsoil samples were extracted by this method in order to minimize the contribution of K from organic matter mineralized in the hot sulfuric acid. 10 gram samples were dispersed in 25 ml of distilled water. After mixing the suspension, 10 ml of concentrated sulfuric acid were added. Another 25 ml of distilled water were added after 30 minutes. Then the samples were filtered and washed with 0.1 N H_2SO_4. K in the three different types of extracts and Na in the NH_4OAc and AgTU extracts were determined with a flame photometer calibrated with standards prepared in the different extractants. Ca and Mg in NH_4OAc and in AgTU extracts were determined with an atomic absorption spectrophotometer.

The acidity was extracted by three extractions with 30 ml of 1 N KCl solution and compared with acidity extracted by the unbuffered AgTU solution. The acidity in the combined KCl extracts was titrated with 0.05 N NaOH using an automatic end point titrator to pH 7. The acidity in the AgTU extracts was determined by titration with 0.01 N NaOH to phenolphthalein end point.

III Results and Discussions

A. Extractable potassium and sodium

The amount of K and Na extracted by NH_4OAc and by AgTU is given in Table 2. The linear correlations for K and Na by both methods are shown in Table 3. The amounts of K and Na extracted by dilute unbuffered AgTU are equal to or considerably higher than the neutral 1 N NH_4OAc-extractable K and Na (Table 2). The results on extractable K correspond with our previous observations on exchangeable K in soils from tropical and from temperate regions (Chhabra et al., 1975; Pleysier and Juo, 1980). Figures 1a and 1b show the amounts of K extracted from the subsoils by H_2SO_4 compared with the NH_4OAc- and with the AgTU-extractable K. The K extracted by AgTU is approximately the same as the K extracted by H_2SO_4 while the NH_4OAc-extractable K is only about half that amount. This indicates that AgTU also extracts some K that is not exchangeable by NH_4OAc. Soils 111-3 and 312-2 were not included in Figures 1a and 1b. These two soils gave extremely high amounts of K in extracts with H_2SO_4. Soil 111 is the only soil containing biotite, a rather easily weatherable K-containing mineral, while soil 312 is a hydromorphic soil containing micas, vermiculite, montmorillonite and kaolinite (Table 1). The high amounts of K extracted from soils 111 and 312 are probably due to dissolution of K-bearing minerals in the hot H_2SO_4.

The results of the clay mineral analysis of the clay fraction of the subsoil samples are given in Table 1. Most soils contain kaolinite as the dominant clay mineral. The soils containing vermiculite release more K and Na by AgTU than by NH_4OAc (Table 2). Previously it was found that soils with illite clay did not show much difference in K extraction by AgTU and by NH_4OAc while montmorillonitic saline and alkali soils gave large differences in extracted K by the two methods (Chhabra et al., 1975). The latter soils also probably contained vermiculite clay. The extra K and Na extracted from various soils by AgTU as compared to NH_4OAc comes probably from interlayer spaces of vermiculite clay.

The presence of vermiculite is often reported as responsible for fixation of K in soils (Page et al., 1967; Rühlicke, 1983; DeMumbrum and Hoover, 1958). The concept of fixation and nonexchangeability of K is rather arbitrary and depends on the method used to displace K. Ammonium acetate is commonly used for this. It would be better to differentiate the extractable K in terms of difficulty or ease of exchange. A similar suggestion was made also by Coulter (1969).

Table 2 shows that soils 138-3, 155-1, SL5-1, SL1-1, ST8-1, N50-1, N50-3 and N53-1 also release considerably more K by AgTU than by NH_4OAc. Soil 138 contains about 80% clay, including kaolinite. Clay minerals were not determined on the other soils.

Because of the good correlation between extractable K by AgTU and by hot H_2SO_4, it should be worthwhile to study the usefulness of the AgTU-extractable K as an index of plant-available soil K.

B. Extractable acidity

1. Effect of charge properties

The acidity extracted by three extractions with 1 N KCl and with 0.01 N AgTU solution is given in Table 2. The correlation between both is shown in Table 3. Rather large differences in acidity extracted by the two extractants are observed for several soils. The soils containing vermiculite in the clay fraction release more acidity by AgTU than by KCl (i.e., soils 84, 312, 296, 185, 305, 111 and 116). The extra acidity extracted from these soils by AgTU as compared to the KCl-extractable acidity is probably due to Al and hydroxy-Al cations from interlayer positions of vermiculite clay. The existence of these interlayer cations in vermiculite was demonstrated by others (Rich, 1960; Page et al., 1965). The very low clay content of soil N55 probably resulted in a limited contribution from vermiculite to the AgTU-exchangeable acidity.

The differences in acidity extracted by AgTU and by KCl from the other soils can be explained in terms of the charge properties of the soils. Kaolinitic soils usually have a mixture of variable and permanent charge properties. These soils can have a net negative, positive or zero charge depending on the pH and on the ionic strength of the soil solution (Figure 2). Soils with a pH above the ZPC (zero point of charge) will have a net negative charge while those with a pH below the ZPC will have a net positive charge. The magnitude of the effect of the ionic strength on the charge depends on the position of the ZPC relative to the soil solution pH and on the type and amount of soil components with variable charge properties. The oxides increase the ZPC of soils while organic matter lowers it (Van Raij and Peech, 1972).

The major difference between the AgTU and KCl extractants is their ionic strength, which is much higher for the KCl than for the AgTU solution. The net charge of soils with a pH above the ZPC will be more negative in 1 N KCl extractant than in 0.01 N AgTU solution. The higher negative charge and charge density in the KCl extractant will result in stronger adsorption of polyvalent cation (i.e., Al and hydroxy-Al), and in re-adsorption of protons on the increased negative charge. These soils will then release more acidity by AgTU than by KCl.

The ZPC of kaolinitic soils is usually below pH 5 (Gallez et al., 1976) and kaolinitic soils with a pH of 5 or above will then release more acidity by AgTU than by KCl (i.e., soils 84-1, 82-1, 82-2, 314-1, 137-1, 187-1, 312-1, 296-1, 185-1, 305-1, 111-1, 116-1, 138-1, 155-1, 71-1, 76-1, 66-1 and ST3-1 (Table 2). All of these soils are surface soils, which illustrates the lowering effect of organic matter on the ZPC. The subsoils are lower in organic matter and are often higher in oxide content and therefore have a higher ZPC than surface soils.

The effect of ionic strength on the charge will be low or even be the opposite when the pH is approaching or is below the ZPC of the soil. The KCl solution will then become as efficient or more efficient as AgTU for extraction of Al and H. This is apparently the case for soils such as soils 119, 117, 150, N51, 310, N50, 151, SL7 and SL1, which have a low pH (less than 5) in surface and subsoil samples (Tables 1 and 2).

The difference in acidity extracted by AgTU and by KCl depends on the organic matter and sesquioxide content of the soil as these affect the position of the ZPC relative to the pH. For example, soil 96 has a very acid surface horizon but the acidity extracted by AgTU and by KCl is approximately the same. This is due to the high organic matter content, which probably lowered the ZPC considerably (Tables 1 and 2). On the other hand, soils 286-1, 286-3, 314-3, 137-2, 188-1, 188-7 and 187-4 have a pH above 5, and less acidity is extracted by AgTU than by KCl (Tables 1 and 2). These are oxic or ferrallitic soils, or soils derived from basaltic material, which contain usually a rather high amount of oxides and have a high ZPC (Gallez et al., 1975; Greenland, 1981; Juo et al., 1974; Keng and Uehara, 1973; Gallez et al., 1976). These soils therefore release less acidity by AgTU than by KCl.

Soils N53-1, N55-2, 96-3, N45-1, ST8-3, 311-3 and 120 have a pH above 5 and also release less acidity by AgTU than by KCl. These soils are all hydromorphic soils. The rather high amounts of soluble iron often found in hydromorphic soils could be an explanation of why some of these soils, after drying, behave like oxic soils with regard to their extractable acidity by AgTU and KCl.

The differences in extracted acidity by AgTU and by KCl change with time and this could indicate that the variable charges (and the ZPC) are affected by the air-dry storage.

The concentration dependence of the extractable acidity in kaolinitic soils partly explains why liming rates calculated on the basis of exchangeable acidity (extracted at high ionic strength) do not always give the expected change in pH and base saturation in the field after liming (Kamprath, 1970; Reeve and Sumner, 1970). Field measurement of acidity of kaolinitic soils extracted at low ionic strength should give more reliable data for calculation of lime application rates. We reported before that the CSSET- method allows one to measure percent base saturation in the field. Lime requirements could be calculated from these field measurements of soil acidity at low ionic strength (Pleysier et al., 1986).

2. Effect of drying and storage.

Various soil properties can be affected by storage and drying. Drying of soil samples increases the solubility and reducing ability of soil organic matter, and this results in a pH increase of the soil. These effects increase with time of storage (Boulding et al., 1971; Bartlett, 1981). This is illustrated in Table 4 which shows the pH in water and the acidity by AgTU and by KCl measured on soil 55, 75, 80, 95, 118, 139 and 79 with an interval of 5 years of air-dry storage. The acidity by KCl tends to increase with time of storage, especially in the subsoil. Table 4 shows also a considerable pH increase with time in the surface soils, while the pH of the subsoil samples (which are lower in organic matter content) remains more or less constant. The pH values for some of the soil samples of Tables 1 and 4 were also reported by others (Greenland, 1981). The pH values reported by Greenland were considerably lower than the pH values given in Tables 1 and 4. The differences become even more significant considering the fact that the pH values reported by Greenland were obtained in a 1:5 soil/water ratio.

C. Extractable calcium and magnesium

The amounts of Ca and Mg extracted by a single extraction with unbuffered AgTU and by three extractions with neutral 1 N NH_4OAc are shown in Table 2. The linear correlations for Ca and Mg by both methods are given in Table 3. There is generally a good agreement between the extracted Ca and Mg by both methods. However, the amounts of Ca and Mg extracted by AgTU are usually somewhat lower than by NH_4OAc. The differences are often larger for Ca than for Mg, and the differences tend to increase with increasing organic matter content and with decreasing pH.

Previous work on acid podzol soils with high organic matter content showed that the same amounts of Ca and Mg were extracted by pH 7 buffered AgTU and by neutral 1 N NH_4OAc (Chhabra et al., 1975). In kaolinitic soils, NH_4OAc extracted slightly higher amounts of Ca than did unbuffered AgTU. Bumbla and McLean (1965) reported also that unbuffered 1 N KCl solution could not extract part of the NH_4OAc (pH 7) exchangeable Ca from acid soils with high organic matter content. These findings indicate that Ca (and to a lesser extent Mg) is easier to extract at pH 7 than at a lower pH. The explanation for this is not clear, but probably involves Ca and Mg adsorbed on pH-dependent charges. The fact that organic matter and also other soil components (i.e., carbonates, sulfates, etc.) are more soluble in neutral 1 N NH_4OAc than in AgTU or in KCl may, for some soils, explain the differences in extractability of Ca and Mg by NH_4OAc pH 7 and by unbuffered AgTU or KCl.

D. Effective CEC

Table 2 shows the effective CEC by NH_4OAc and KCl and the effective CEC by AgTU. The latter is the sum of exchangeable bases and acidity extracted with unbuffered AgTU. A good correlation is obtained for the effective CEC values by both methods (Table 3). The effective CEC by AgTU is usually slightly lower than the effective CEC by NH_4OAc and KCl. The differences are mainly due to the differences in extraction of Ca and Mg by NH_4OAc pH 7 and by unbuffered AgTU as discussed above.

IV Conclusions

A good agreement exists between exchangeable cations determined by the AgTU method and by the NH_4AOc and KCl methods. When vermiculite clay is present in the soil, the amounts of K and Na extracted by the unbuffered AgTU solution are higher than the amounts extracted by three extractions with 1 N NH_4OAc at pH 7 . More Al+H is then also extracted by AgTU than by 1 N KCl. The extra K, Na and Al+H extracted by AgTU from these soils probably comes from the vermiculite interlayer sites. The AgTU solution extracts about the same amounts of K from subsoil samples as is extracted by hot H_2SO_4.

The extractable acidity is affected by the concentration of the unbuffered extracting solution. The difference in acidity extracted by 0.01 N AgTU and by 1 N KCl depends on the position of the ZPC relative to the pH of the soil.

Air-dry storage of soils can result in a pH increase (especially in the organic-rich surface soils) and in a change in extractable acidity. The acidity extracted by AgTU decreases while the acidity extracted by KCl tends to increase with time of storage.

Unbuffered AgTU often extracts somewhat less Ca and Mg from acid soils than is extracted by neutral 1 N NH_4OAc. The effective CEC by AgTU correlates well with the effective CEC by KCl and NH_4OAc. Deviations are mainly due to differences in extractability of Ca and Mg.

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Table 1: Some properties of the soils used in this study.

Soil No	Horizon	Classification	pH	% O.C.	% Clay	Clay Minerals
286-1	A_1	N.C.	5.4	2.15	56.1	-
286-3	B_2	N.C.	5.0	1.11	69.7	K
84-1	A_1	Vertic Tropaquept	5.9	0.76	5.2	-
84-4	C_1	" "	6.2	0.20	39.6	K, V
82-1	A_1	Oxic Haplustalf	6.5	2.94	17.2	-
82-2	A_3	" "	5.7	0.84	11.6	K, Q
310-1	A_p	Typic Tropaquept	4.8	0.69	11.2	-
310-4	B	" "	4.7	0.27	13.2	K, Q
311-1	A_p	Psamm. Tropaquent	4.8	0.82	5.2	-
311-3	B_2	" "	5.5	0.18	5.6	K, G, Q
312-1	A_1	Aquic Ustifluvent	5.7	0.33	51.6	-
312-2	B_2	" "	6.0	0.64	53.6	K, M, V, Mi 1
314-1	A_1	Oxic Haplustalf	6.4	0.57	5.6	-
314-3	B_{2t}	" "	6.2	0.22	33.2	K, Q
296-1	A_p	N.C.	5.0	1.42	50.2	-
296-3	B_3	N.C.	5.8	0.50	49.6	K, V, Q
297-1	A_p	Plintic Tropaquult	4.9	0.81	37.6	-
297-3	B_2	" "	4.7	0.29	37.2	K, V, Q
185-1	A_1	N.C.	7.3	1.04	43.6	-
185-7	B	N.C.	8.5	0.32	43.6	K, V, Q
137-1	A	N.C.	5.5	1.26	56.1	-
137-2	B	N.C.	5.4	0.98	57.6	K
187-1	A_p	N.C.	5.3	0.10	7.6	-
187-4	B	N.C.	5.3	0.24	13.6	K, M, Q
188-1	A	N.C.	5.8	0.10	7.6	-
188-7	Bt	N.C.	5.0	0.13	15.2	K, M, Q
305-1	A_p	Typic Tropaquept	4.9	4.54	58.0	-
305-3	C_1	" "	6.0	0.78	75.6	K, V, Q
105-1	A_1	N.C.	7.0	0.37	7.2	-
105-3	B_{2t}	N.C.	6.2	0.24	19.2	K, Q
111-1	A_{11}	N.C.	6.6	1.63	16.9	-
111-3	B	N.C.	6.5	0.73	27.6	K, V, Mi 2
116-1	A	N.C.	7.0	1.65	38.4	-
116-2	B	N.C.	7.4	0.97	37.6	V, M, Q
117-1	A_1	N.C.	4.6	1.97	12.9	-
117-3	B_t	N.C.	4.5	0.93	45.6	K
119-1	A_1	N.C.	4.3	1.07	17.6	-
119-4	B_{22t}	N.C.	4.2	0.49	29.6	K
120-1	A_{11}	N.C.	5.5	1.52	30.6	-
120-3	B_2	N.C.	4.6	0.60	35.6	K, Q, G
138-1	A_1	N.C.	6.1	2.12	78.0	-
138-3	B_2	N.C.	4.6	1.21	75.7	K
151-1	A_1	N.C.	3.9	7.38	85.5	-
151-5	B_{22}	N.C.	4.4	0.15	-	K, Goe
155-1	A_1	Typic Vidrandept	6.1	6.50	9.2	-
155-2	C	" "	7.1	0.44	-	-
155-3	A	" "	5.3	7.90	-	-
155-4	B	" "	5.4	2.41	-	-
71-1	A_p	Orthoxic Tropudult	5.7	4.80	22.7	-
71-5	B_{22t}	" "	4.4	0.29	31.2	K
76-1	A_1	Oxic Rhodustalf	5.9	7.38	42.7	-
76-3	B_{2t}	" "	5.6	0.55	47.6	K, Mi 1
11-1	A		6.6	0.49	9.6	-
11-4	B_{2t}		4.9	0.19	39.6	K

Table 1 cont'd

Soil No	Horizon	Classification	pH	% O.C.	% Clay	Clay Minerals
66-1	A_1	Aquentic Ustortent	6.8	0.68	5.2	-
66-3	C_1	" "	6.4	0.28	11.2	K, M, Q
150-2	A_1	N.C.	4.4	1.48	-	-
150-5	B_{22}	N.C.	4.1	0.65	-	-
96-1	A_1	Aeric Tropaquent	4.5	5.08	11.4	-
96-3	C_{1g}	" "	5.3	0.28	7.2	K, Q, G
SL5-1	A_p	N.C.	4.3	5.70	33.0	-
SL5-2	B	N.C.	4.2	1.30	47.0	-
SL7-1	A_p	Plinthic Tropaquult	4.7	3.17	11.0	-
SL7-3	B_2	" "	4.6	0.10	15.0	-
SL1-1	A_{pg}	Typic Tropaquept	4.5	2.15	3.0	-
SL1-3	B_{3g}	" "	4.6	0.22	5.0	-
ST8-1	A_1	N.C.	-	3.48	-	-
ST8-3	B	N.C.	5.0	0.10	-	-
ST3-1	A_1	N.C.	6.1	3.08	-	-
ST3-3	A_1	N.C.	4.9	0.40	-	-
N50-1	A_p	Aeric Tropaquept	4.9	2.05	-	-
N50-3	B_2	" "	4.9	0.47	-	-
N45-1	A_1	Typic Distropept	5.4	1.41	-	-
N45-4	B_2	" "	4.6	0.47	-	-
N55-1	A_{1g}	Typic Tropaquent	6.1	0.30	9.6	-
N55-2	C_g	" "	6.6	0.23	11.6	K, V, Q
N51-1	A_1	Typic Paleudult	4.4	1.61	17.2	-
N51-5	IIB	" "	4.3	0.27	33.6	K
N53-1	A_{1g}	Typic Ustipsamment	5.4	1.76	11.0	-
N53-2	B	" "	4.5	0.25	9.6	K, M, Q

N.C.: not classified.
K: kaolinite; M: montmorillonite; V: vermiculite; Q: quartz; Mi 1: mica's (illite or muscovite); Mi 2: mica's (biotite); G: gibbsite; Goe: goethite.
The clay minerals are given in order of decreasing abundance.

Table 2. Exchangeable bases, total acidity (TA) and ECEC values by NH_4OAc-KCl (1) and by AgTu (2) (me/100 g)

Soil No.	Ca 1	Ca 2	Mg 1	Mg 2	K 1	K 2	Na 1	Na 2	TA 1	TA 2	ECEC 1	ECEC 2
286-1	4.16	2.47	1.08	1.92	0.27	0.24	0.04	0.07	0.56	0.32	6.11	5.02
286-3	1.56	1.51	0.81	0.68	0.08	0.13	0.03	0.05	1.03	0.98	3.51	3.35
84-1	6.16	3.01	2.16	1.65	0.22	0.25	0.15	0.17	0.16	0.22	8.85	5.30
84-4	16.38	15.35	11.13	9.78	0.35	0.60	0.43	0.59	0.22	0.57	28.51	26.89
82-1	12.02	5.44	3.21	2.21	0.59	0.52	0.08	0.10	0.19	0.37	16.09	8.64
82-2	1.51	1.01	0.95	0.73	0.10	0.11	0.03	0.04	0.37	1.17	2.96	3.06
310-1	0.79	0.65	0.16	0.19	0.07	0.10	0.06	0.07	0.81	0.54	1.89	1.55
310-4	0.33	0.25	0.09	0.10	0.03	0.04	0.02	0.02	0.80	0.44	1.27	0.85
311-1	0.36	0.21	0.08	0.08	0.05	0.07	0.05	0.04	0.79	0.54	1.33	0.94
311-3	0.09	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.48	0.18	0.62	0.23
312-1	7.65	7.86	5.83	5.05	0.39	0.44	0.78	0.96	0.38	0.81	15.03	15.12
312-2	8.15	7.07	5.83	5.25	0.27	0.44	0.54	0.71	0.40	0.84	15.09	14.31
314-1	2.09	1.34	0.67	0.42	0.17	0.19	0.04	0.04	0.14	0.16	3.11	2.15
314-3	2.08	1.93	1.10	0.88	0.13	0.13	0.04	0.05	0.33	0.17	3.68	3.16
296-1	5.81	6.49	7.24	7.59	0.35	0.48	0.15	0.24	0.76	0.85	14.31	15.65
296-3	6.92	7.05	9.13	10.15	0.32	0.40	0.19	0.26	0.36	0.69	16.92	18.55
297-1	1.63	1.42	1.18	0.93	0.13	0.13	0.05	0.06	0.89	0.55	3.88	3.09
297-3	0.65	0.00	1.92	1.80	0.10	0.13	0.05	0.07	4.73	4.91	7.45	6.91
185-1	24.90	25.99	11.27	8.74	0.46	0.92	0.12	0.49	0.21	2.10	36.96	38.24
185-7	23.30	21.14	19.17	15.41	0.45	1.01	0.50	2.30	0.00	1.62	43.42	41.48
137-1	9.27	6.04	3.97	3.00	0.61	0.68	0.09	0.19	0.34	0.64	14.28	10.55
137-2	7.57	6.74	4.69	4.60	0.39	0.47	0.12	0.17	1.31	0.84	14.08	12.82
187-1	1.23	1.53	1.76	0.76	0.10	0.15	0.04	0.07	0.56	0.65	3.69	3.16
187-4	3.09	3.29	2.42	1.27	0.07	0.05	0.04	0.11	0.99	0.76	6.61	5.47
188-1	0.72	1.50	0.35	0.34	0.17	0.21	0.02	0.04	0.37	0.16	1.63	2.25
188-7	1.18	1.47	1.22	1.06	0.10	0.09	0.03	0.04	0.87	0.32	3.40	2.98
305-1	25.90	25.83	6.80	5.65	0.40	0.52	0.13	0.23	0.75	1.36	33.98	33.59
305-3	30.36	29.34	6.90	5.46	0.25	0.56	0.10	0.23	0.38	0.82	37.99	36.41
105-1	2.23	1.68	1.40	0.90	0.20	0.21	0.04	0.04	0.30	0.20	4.17	3.03
105-3	1.10	0.80	0.97	0.64	0.03	0.02	0.03	0.03	0.49	0.12	2.62	1.61
111-1	8.86	6.36	3.25	2.88	2.13	2.30	0.13	0.23	0.33	0.91	14.70	12.68
111-3	6.77	5.80	3.97	3.60	0.43	0.70	0.16	0.26	0.33	0.67	11.66	11.03
116-1	15.84	12.92	9.53	9.01	0.19	0.45	0.86	1.08	0.69	1.14	27.11	24.60
116-2	15.89	14.68	11.48	9.96	0.08	0.54	1.79	1.52	0.01	1.35	29.25	28.05
117-1	2.12	2.09	0.86	0.81	0.76	0.78	0.07	0.09	1.52	0.93	5.33	4.70
117-3	0.44	0.08	0.12	0.13	0.15	0.16	0.05	0.08	2.57	1.63	3.33	2.18

Table 2. cont'd.

Soil No.	Ca 1	Ca 2	Mg 1	Mg 2	K 1	K 2	Na 1	Na 2	TA 1	TA 2	ECEC 1	ECEC 2
119-1	0.75	0.34	0.21	0.19	0.42	0.36	0.09	0.07	1.60	0.75	3.07	1.71
119-4	0.18	0.00	0.14	0.15	0.09	0.08	0.05	0.05	1.44	1.32	1.90	1.60
120-1	0.93	0.48	0.63	0.37	0.33	0.29	0.07	0.08	0.08	0.68	2.76	1.90
120-3	0.65	0.37	0.71	0.53	0.17	0.19	0.07	0.08	1.34	0.93	2.94	2.10
138-1	5.42	3.17	5.19	4.13	1.23	1.05	0.11	0.15	0.40	0.46	12.35	8.86
138-3	0.73	1.83	0.78	1.97	0.15	0.64	0.04	0.07	2.42	0.20	4.12	4.71
151-1	0.74	0.03	0.81	0.52	0.23	0.27	0.13	0.15	4.76	3.45	6.67	4.42
151-5	0.07	0.00	0.02	0.01	0.03	0.04	0.03	0.04	2.26	2.10	2.41	2.19
155-1	13.57	13.46	4.97	6.39	1.97	2.88	0.21	0.51	0.74	0.87	21.46	24.11
155-2	0.91	0.20	0.42	0.13	0.10	0.05	0.26	0.24	0.06	0.11	1.75	0.73
155-3	9.78	2.81	4.86	2.25	0.31	0.23	0.08	0.11	0.88	0.69	15.91	6.09
155-4	1.52	1.03	1.90	1.73	0.09	0.21	0.05	0.07	0.37	0.22	3.39	3.26
71-1	11.28	6.39	5.27	3.95	0.78	0.86	0.07	0.16	0.28	1.44	17.68	12.80
71-5	0.53	0.00	0.16	0.19	0.14	0.19	0.02	0.04	2.21	2.16	3.06	2.58
76-1	49.76	26.05	7.82	6.91	0.92	1.03	0.09	0.32	0.20	1.44	58.79	35.75
76-3	5.59	3.82	2.95	2.59	0.16	0.14	0.05	0.11	0.30	0.40	9.05	7.06
11-1	2.34	1.44	0.66	0.49	0.33	0.40	0.04	0.08	0.18	0.14	3.55	2.55
11-4	1.60	1.23	0.81	0.80	0.21	0.35	0.07	0.12	3.79	0.38	6.48	2.88
66-1	2.87	1.86	0.94	0.69	0.56	0.40	0.03	0.05	0.19	0.24	4.59	3.24
66-3	1.10	0.73	0.65	0.52	0.14	0.13	0.03	0.03	0.15	0.09	2.07	1.50
150-2	0.20	0.00	0.04	0.05	0.06	0.06	0.03	0.04	1.93	1.14	2.26	1.29
150-5	0.16	0.00	0.03	0.03	0.07	0.06	0.03	0.05	1.80	1.29	2.09	1.43
96-1	5.64	3.94	1.43	1.56	0.30	0.48	0.05	0.10	1.23	1.34	8.65	7.42
96-3	0.16	0.01	0.04	0.04	0.11	0.05	0.01	0.02	0.84	0.47	1.16	0.59
SL5-1	1.85	1.05	1.27	1.32	0.09	0.22	0.04	0.09	5.15	3.60	8.40	6.28
SL5-2	0.95	0.80	1.23	1.40	0.07	0.18	0.06	0.11	5.34	6.05	7.65	8.54
SL7-1	0.28	0.00	0.09	0.07	0.06	0.12	0.02	0.04	3.65	2.90	4.10	3.13
SL7-3	0.18	0.00	0.09	0.08	0.03	0.10	0.01	0.04	3.43	1.97	3.74	2.19
SL1-1	0.33	0.02	0.08	0.12	0.06	0.37	0.02	0.04	2.76	1.31	3.25	1.86
SL1-3	0.23	0.12	0.07	0.14	0.02	0.09	0.01	0.03	2.36	1.58	2.69	1.96
ST8-1	3.78	8.14	1.07	1.33	0.38	0.64	0.07	0.10	1.82	0.71	7.08	10.92
ST8-3	0.17	0.46	0.07	0.12	0.07	0.02	0.04	0.04	1.08	0.21	1.43	0.85
ST3-1	0.56	13.66	8.72	5.86	0.31	0.22	0.07	0.12	0.00	0.52	9.66	20.38
ST3-3	2.00	1.81	0.57	0.67	0.05	0.07	0.03	0.05	1.40	0.25	4.05	2.35

Table 2. cont'd.

Soil No.	Ca 1	Ca 2	Mg 1	Mg 2	K 1	K 2	Na 1	Na 2	TA 1	TA 2	ECEC 1	ECEC 2
N50-1	25.45	35.63	6.34	2.80	0.19	0.63	0.06	0.26	2.97	2.02	35.01	41.34
N50-3	6.44	8.58	3.78	3.95	0.20	0.45	0.05	0.15	4.10	3.01	14.57	16.14
N45-1	2.74	2.99	1.17	0.59	0.18	0.18	0.03	0.05	1.20	0.43	5.32	4.24
N45-4	0.20	0.00	0.14	0.10	0.07	0.13	0.02	0.05	4.97	4.20	5.40	4.48
N55-1	2.05	1.59	0.90	0.84	0.10	0.18	0.03	0.06	1.21	0.20	4.29	2.87
N55-2	3.79	3.44	1.38	1.56	0.15	0.25	0.15	0.19	0.35	0.23	5.82	5.67
N51-1	0.85	1.07	0.28	0.26	0.07	0.08	0.02	0.03	2.23	1.02	3.45	2.46
N51-5	0.16	0.00	0.05	0.06	0.04	0.04	0.01	0.02	2.47	1.62	2.73	1.74
N53-1	4.69	5.74	1.68	2.06	0.25	0.50	0.64	1.95	0.40	0.28	7.66	10.53
N53-2	1.75	1.52	0.73	0.70	0.09	0.16	0.08	0.41	1.15	0.63	2.80	3.42

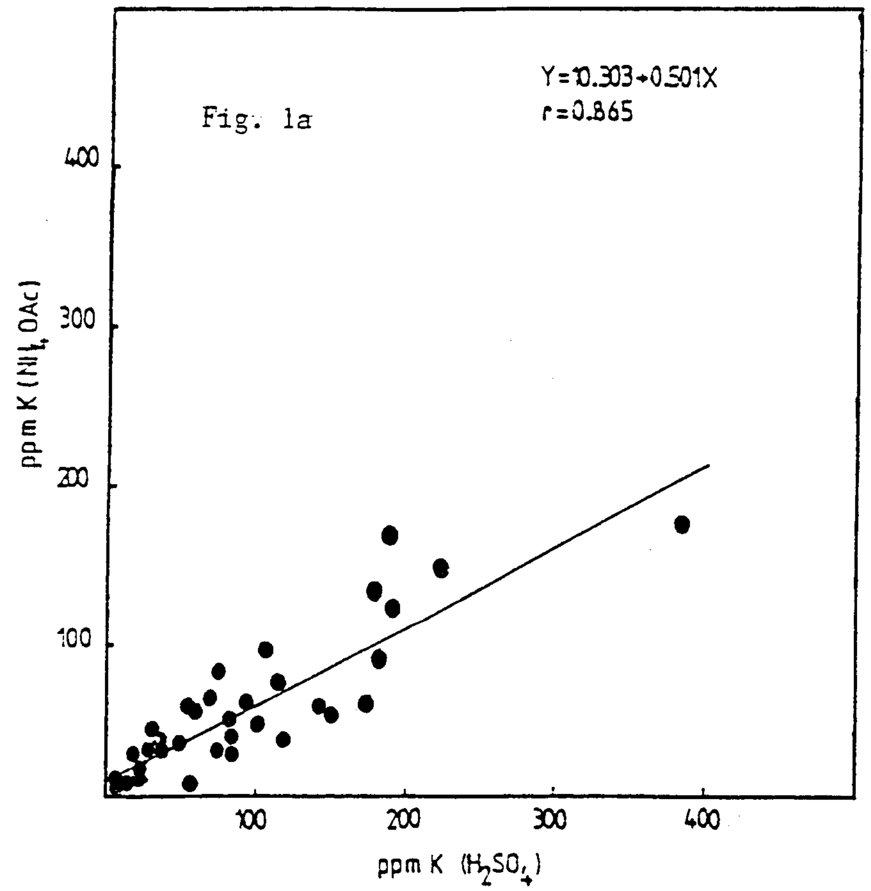
Table 3: Linear regression equations and correlations between exchangeable cations by AgTU(Y) and by NH_4OAc-KCl(X); and between ECEC by AgTU(Y) and ECEC by NH_4OAc-KCl(X).

Exchangeable cations, ECEC me/100 g	Linear regression	R
K	Y = 0.048 + 1.132 X	0.931
Na	Y = 0.053 + 1.247 X	0.783
Al+H	Y = 0.221 + 0.654 X	0.812
Ca	Y = 0.343 + 0.803 X	0.910
Mg	Y = 0.036 + 0.848 X	0.970
ECEC	Y = 0.100 + 0.896 X	0.954

Table 4: Effect of 5 year air-dry storage of soils on pH(1:1) in water and on extractable acidity (Al+H) by 0.01 molar AgTU and by three extractions with molar KCl.

Soil No	1984			1979*		
	$pH(1:1)_w$	(Al+H) me/100g		$pH(1:1)_w$	(Al+H) me/100g	
		AgTU	KCl		AgTU	KCl
55-1	6.7	0.55	0.17	5.7	0.86	0.10
55-4	5.8	0.20	0.23	5.8	0.65	0.05
75-1	6.7	1.16	0.12	6.5	0.75	0.24
75-3	5.6	0.51	0.45	5.8	1.19	0.20
80-2	6.6	0.42	0.25	5.8	0.87	0.08
80-5	5.3	0.15	0.24	5.2	0.77	0
95-1	4.3	1.79	2.37	4.0	3.18	2.84
118-1	4.9	0.84	1.77	4.2	2.15	2.28
118-4	4.5	2.07	2.77	4.5	3.62	2.16
139-1	6.3	0.37	0.36	6.0	0.50	0.08
139-4	5.6	0.30	0.34	5.6	0.47	0.08
79-1	6.1	0.26	0.53	5.2	0.84	0.14

*) Pleysier & Juo. Soil Sci. 1980.



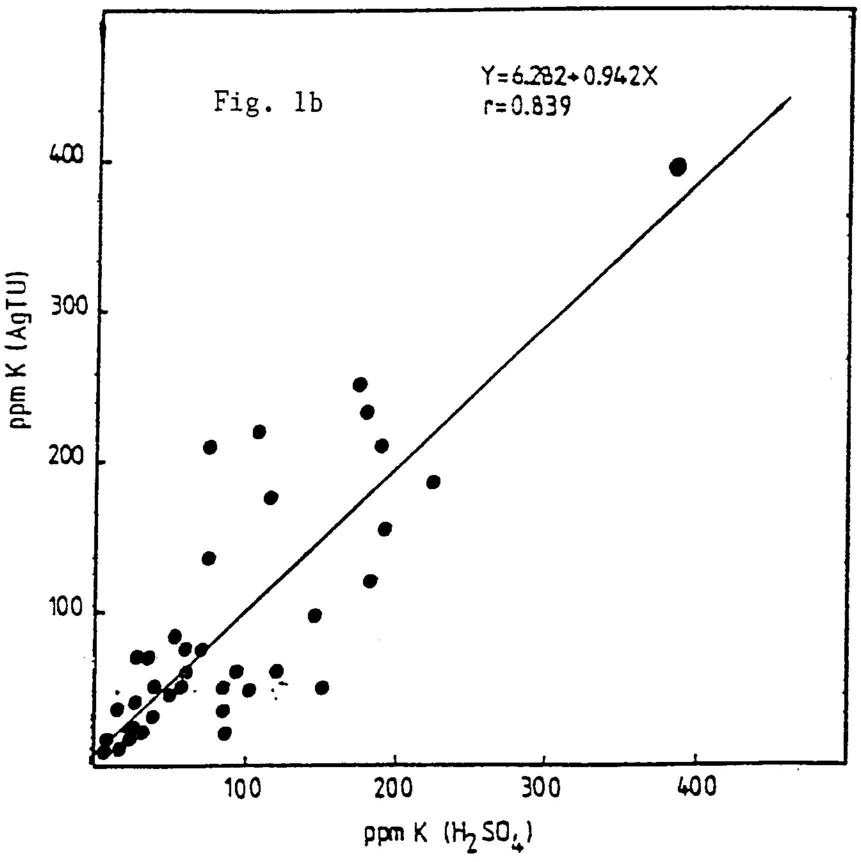


Figure 1a: Comparison of extractable K by dilute H_2SO_4 and by neutral molar NH_4OAc

Figure 1b: Comparison of extractable K by dilute H_2SO_4 and by unbuffered 10^{-2}mol L^{-1}AgTU.

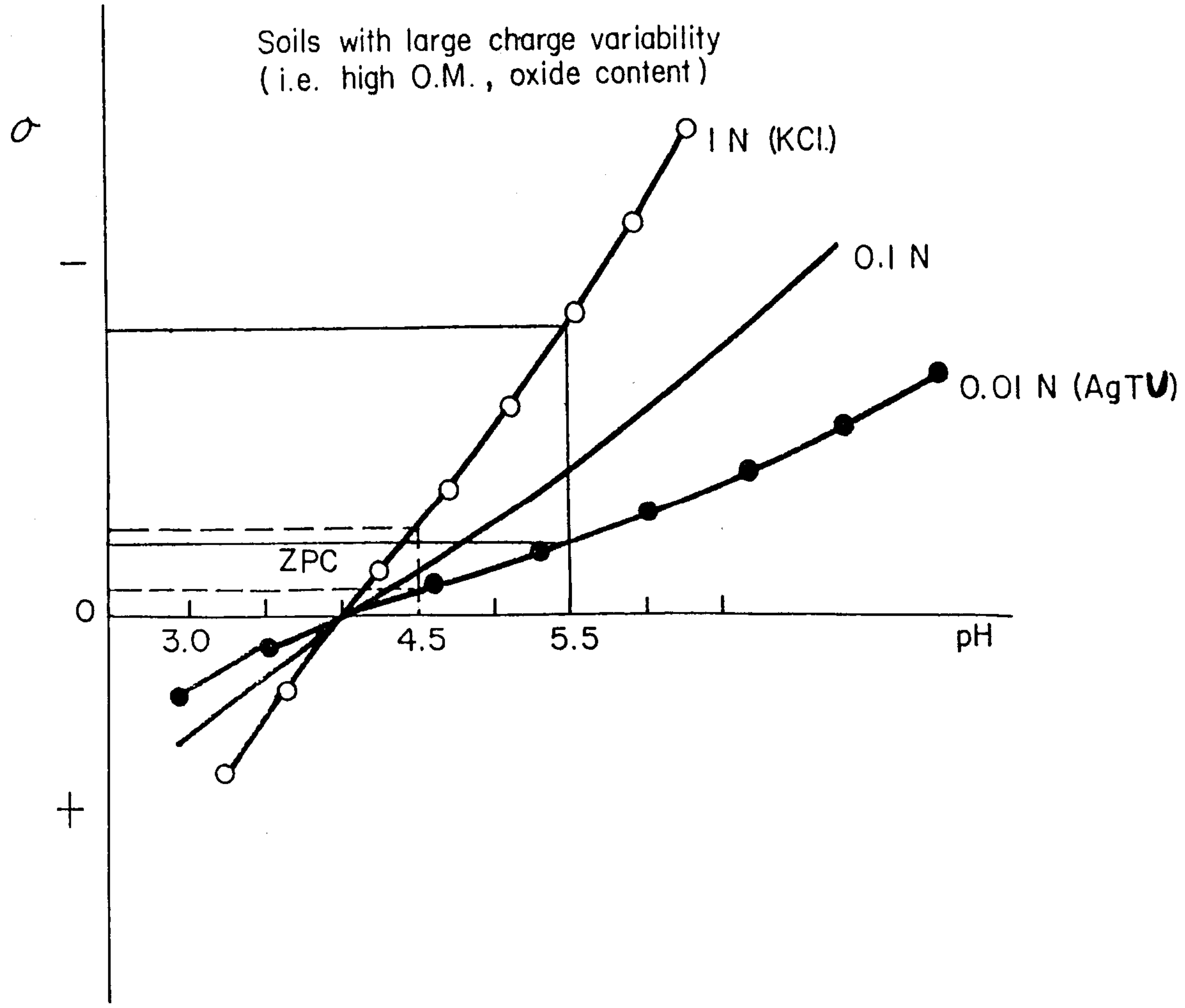


Figure 2: Effect of extractants on variable charge

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AN EVALUATION OF AUTOMATED AND MANUAL METHODS FOR NH_4-N ANALYSIS IN THE DETERMINATION OF CATION EXCHANGE CAPACITY OF SOILS

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ABSTRACT

Cation exchange capacity (CEC) is an important and commonly used measurement in the analysis of soils. One of the most widely used methods for CEC involves saturation of the exchange sites with NH_4 (as 1.0 N NH_4OAc, pH 7.0), followed by the displacement of the NH_4 by another salt solution and the determination of NH_4 in the resulting extract. Twenty soil samples from nine countries (including Labex round 85-1 soil samples) were analyzed. The samples varied in their textures and organic matter content. Two automated methods of NH_4 determination were compared with the traditional macro-Kjeldahl technique. The two automated methods tested were the colorimetric (AutoAnalyzer) and the distillation (Kjeltec) procedures. The CEC of the soils ranged from 1.33 to 123 meq 100 g^{-1} (cmol kg^{-1}). There were no significant differences among the three methods tested; therefore, any one of the techniques can be used for the determination of NH_4 for CEC. The advantages and disadvantages of these methods are discussed.

I Introduction

Cation exchange capacity (CEC) is an important and commonly used measurement in the analysis of soils. It is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil (Rhodes, 1982). To a large degree, CEC determines the level of soil fertility (Wilde et al., 1979). One of the most widely used methods for CEC (Atkinson et al., 1958) involves saturation of the exchange sites with an index cation (such as NH_4 using 1.0 N NH_4OAc, pH 7.0), followed by the displacement of the NH_4 by another salt solution and the determination of NH_4 (that had been adsorbed by the soil) in the resulting extract. It is most frequently determined by the Kjeldahl distillation technique (Chapman and Pratt, 1961; Jackson, 1958). The literature on the conventional Kjeldahl determination is voluminous.

Automated colorimetric methods have been used by several investigators for the determination of NH_4 in Kjeldahl digests of soils (Schuman et al., 1973; Skjemstad and Reeve, 1976) and in solutions containing widely differing amounts of organic and inorganic compounds (Johnson and Edwards, 1979; Verry and Timmons, 1977; White and Gosz, 1981).

An automated distillation-titration method utilizing the Kjeltec Auto 1030 Analyzer, based on the Kjeldahl procedure, has been used for the determination of nitrogen in plant samples. However, this technique has not been evaluated for NH_4 analysis in the NaCl leachates for the determination of CEC (Ola Hult, Technical Manager, Tecator AB, Höganäs, Sweden: personal communication, 1985).

The present study was undertaken to compare the automated colorimetric method and the automated distillation and titration method against the conventional Kjeldahl procedure for NH_4-N analysis to determine CEC of soils.

II Materials and Methods

a. Soils

Twenty soil samples were used for this investigation (Table 1). They were selected to obtain a range in pH, organic carbon content and texture. Samples 1-17 had been used earlier for inter-laboratory check sample studies carried out by different organizations as shown in Table 1. The last three samples (No. 18-20) were air dried, ground to pass through a 2-mm sieve and mixed thoroughly.

b. Soils Characterization

The pH was determined on a soil paste (US Salinity Laboratory Staff 1954). Organic carbon was determined by the Walkley-Black titrimetric wet oxidation method (Greweling and Peech, 1965). Particle-size analysis was performed by the Bouyoucos hydrometer sedimentation technique (Day, 1965). These properties of the soils are presented in Table 2.

c. Extraction

The extraction was performed according to the procedure given by Atkinson et al. (1958). Approximately 50 ml of 1.0 N NH_4OAc (pH 7.0) were added to a 25.0 g soil sample (10.0 g organic soil) in a 250 ml beaker. After stirring, the samples were allowed to stand overnight. Samples were filtered with gentle suction through a Nalgene Buchner funnel (Whatman #42 filter paper, 7.0 cm). Small portions of NH_4OAc solution were used for leaching, draining well between each addition. The leachate (approximately 250 ml) was discarded. Excess NH_4OAc from NH_4-saturated soil was leached with 200 ml 95% C_2H_5OH, using small volumes. The leachate was discarded. The alcohol-washed soil was leached with 10% acidified NaCl solution (0.005 N with respect to acidity) in increments. The leachate was washed into a 250 ml volumetric flask, made up to volume with NaCl and mixed well. All the extractions were done in triplicate.

d. Chemical Analysis

Ammonium-N in the leachate was determined by the Kjeldahl procedure, Auto-Analyzer technique, and Kjeltec 1030 Auto Analyzer.

Kjeldahl Method: The NaCl leachate (100 ml) was transferred to an 800 ml Kjeldahl flask and diluted with approximately 300 ml water. After the addition of 10 ml 40% NaOH solution, the NH_3 liberated by distillation was collected in approximately 25 ml of 4% boric acid solution containing N-point indicator. The resulting $NH_4H_2BO_3$ was titrated with standard H_2SO_4 to a pink end point.

AutoAnalyzer Technique: The NaCl leachate was diluted 10 times. A set of 5, 10, 15, 20, 25, 50, 75 and 100 ppm NH_4-N (as $(NH_4)_2SO_4$) were prepared. Ammonia was determined by a Technicon AutoAnalyzer. The flow diagram of the AutoAnalyzer and the manifold are shown in Figure 1. The set up was similar to that of Technicon Instrument Corporation Industrial Method 154-71W (1973).

Kjeltec Auto 1030 Analyzer Technique: The alkali pump was adjusted to deliver 10 ml 40% NaOH solution (Tecator, 1985). An aliquot (100 ml) of the NaCl leachate was transferred to the distillation vessel. The distilled NH_3 was collected into 25 ml 1% boric acid solution containing a mixed indicator methyl red and bromo-cresol green. The titration was performed with standard HCl.

III Results and Discussion

Cation exchange capacity is dependent on soil organic matter and texture. In mineral soils, the clay fraction is largely responsible for cation exchange properties. Therefore, mineral soils were selected to obtain a range in pH (4.8-10.3), organic carbon content (0.14-6.9%), and texture (5-69% sand, 3-68% silt and 18-79% clay). In addition, an organic soil (pH 3.5, organic carbon 48%) was also used.

The CEC of the soils ranged from 1.33 to 123 meq 100 g^{-1} (Table 3). In Table 3, the standard deviations show good precision in all the three methods. Although there was a wide range in the coefficient of variation values for Kjeldahl (0.6-21.2), AutoAnalyzer (0.9-26.8) and Kjeltec system (0.4-17.1), most of the values were less than 5%. It must be pointed out that the triplicate analyses were on three different sub-samples of each soil. Therefore, some of the variation between replicates is probably due to the natural variability found in soils.

There was no significant difference in the CEC (Table 4) among the three methods ($P < 0.05$, two-way ANOVA, SAS Institute Inc., 1985). The three methods were not affected by the various soil types, over a wide range of pH's, CEC, organic carbon and texture. Similarly, automated methods have been reported to give results that do not differ significantly from the accepted Kjeldahl method on water samples (American Public Health Association 1985).

The Kjeldahl procedure is a reliable technique that has provided excellent reproducibility over time for N determination (Bremner and Mulvaney, 1982). The limitations are that it is a cumbersome, time- and labor-intensive technique that can be subject to serious error during certain steps of the analytical procedure.

The AutoAnalyzer is a simple, easy-to-operate instrument. It permits an automated uniform mixing of small precise volumes of the sample solutions and reagents. The technique is very sensitive (set up in Fig. 1 for 0-0.14 ppm NH_4-N). The reduction in the amounts of glassware and reagents required lowers the cost of analysis. Since the analyses can be performed rapidly (40 samples/hr), it enables the laboratory a high sample throughput in routine operation. The instrument does not need the operator to be there constantly. The limitation of the technique is that the time required for set-up and cleanup procedures is greater than the other two techniques.

Generally, NH_4 in soil extracts has been determined in a two-step procedure involving distillation and colorimetric techniques (Bremmer and Mulvaney, 1982; Kempers, 1974). In our investigation NH_4 was determined by the AutoAnalyzer directly in the NaCl leachates, thus eliminating the distillation step. Similarly, NH_4-N in 2 $\underline{M}$ KCl soil extracts has been analyzed directly rather than in distillates by the AutoAnalyzer (Keeny and Nelson, 1982).

The Kjeltec Auto 1030 Analyzer is a part of the Kjeltec Auto Systems. It has been used for fast and automatic distillation, titration and calculation for the determination of protein in plant samples. It uses microcomputer technology for instrument control and for data processing. Receiving solution (H_3BO_3) is dispensed automatically into the titration vessel. Similarly, a preset volume of 40% NaOH solution is pumped into the sample. Titration with a standard HCl solution following the distillation step is performed automatically; a dual photocell system continually sensing the color of the indicator. After completion of the analysis cycle, the instrument is reset automatically for the next sample. Also, the distillation residues are automatically evacuated. This eliminates the handling of hot caustic solution, thus ensuring maximum operator safety. Automatic titration eliminates the subjective error of obtaining the end point manually in the Kjeldahl method. The technique requires two minutes for distillation, titration and presentation of results. The measuring range is 1-160 mg N with a recovery of 99.5-100% (Hjalmarsson and Mindel, 1981). A water saving system reduces the cost of operation compared to the Kjeldahl system. Although in the Kjeldahl method there is a likelihood of NH_3 loss if the flask is not connected to the distillation set up immediately after the alkali addition, we did not experience this problem. Moreover, this problem is eliminated in the Kjeltec system as the alkali is added in a closed system. A limitation of the Kjeltec technique is that the operator has to be present with the equipment as in the Kjeldahls procedure.

Both the AutoAnalyzer and Kjeltec methods are suitable for routine measurements of CEC of soils over a wide pH, organic C and textural ranges. They are rapid, precise, safe and accurate. Experience in our laboratory has shown that it is possible to perform 250 and 125 analyses by the AutoAnalyer and Kjeltec techniques, respectively, in a normal working day compared to only 45 analyses by the Kjeldahl method. In addition, both automated systems are compact and, therefore, require less space then the macro- Kjeldahl unit. The Kjeltec technique would be preferred for smaller workloads of soil high in CEC while the AutoAnalyzer is preferred for larger workloads.

IV Acknowledgements

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Table 1. Soil samples selected for the present study.

No.	Sample		Reference
1	CSSC 9	Canada Soil Survey Committee, Ottawa, Ontario, Canada	McKeague et al. (1978)
2	CSSC 13		
3	WEALA 1	Western Enviro-Agricultural Laboratory Association, Edmonton, Alberta, Canada	Kalra and Peters (1981)
4	WEALA 3		
5	WEALA 6		
6	Utah 1	Utah State University, Logan, Utah, USA	James (1984) *
7	Utah 2		
8	Utah 3		
9	WEALA Research 1		Sandberg (1984)**
10	WEALA Saskatchewan 2		
11	Labex 11 (Syria)	Laboratory Exchange Program, Wageningen, the Netherlands	Pleijsier (1985)
12	Labex 14 (Malaysia)		
13	Labex 15 (Hungary)		
14	Labex 17 (Kenya)		
15	Labex 23 (France)		
16	Labex 26 (Brazil)		
17	Labex 28 (Netherlands)		
18	Kananaskis Provincial Park, Alberta, Canada		
19	Banff, Banff National Park, Alberta, Canada		
20	Mt. Norquay, Banff National Park, Alberta, Canada		

* D.W. James, Utah State University, Logan, Utah, USA (Personal communication).

** P. Sandberg, Alberta Soil and Feed Analysis Ltd., Lethbridge, Alberta, Canada (Personal communication).

Table 2. Some characteristics of the soils used.

Sample No.	pH (water)	Organic carbon	Sand 0.05-2.00 mm	Silt 0.002-0.05 mm	Clay 0.002 mm	Textural class
		%				
1	8.3	0.20	48	29	23	L
2	3.5	48.0	-	-	-	organic
3	8.1	2.01	21	38	41	C
4	6.1	0.50	40	40	20	L
5	5.3	6.97	34	46	20	L
6	5.5	2.90	36	38	26	L
7	7.4	2.38	18	48	34	SiCL
8	7.6	1.45	14	34	52	C
9	7.4	1.57	38	30	32	CL
10	8.0	3.09	68	14	18	SL
11*	7.8	0.14	29	34	34	CL
12	4.8	0.34	62	3	35	SCL
13	10.3	0.26	43	27	29	CL
14	7.9	1.71	5	15	79	C
15	8.0	1.85	35	33	32	CL
16	4.9	0.20	69	5	26	SCL
17	6.8	0.20	14	68	19	SiL
18	7.1	2.31	46	36	18	L
19	7.8	-	-	-	-	-
20	7.5	5.30	37	42	21	L

* Samples 11-17: Median-1 values as given in a report by Pleijsier (1985). This median is the "half-way value" i.e., the number of laboratories reporting a lower value than the median equals those reporting higher values.

Table 3. The mean*, standard edviation and coefficient of variation of cation exchange capacity of soils**.

Sample	Kjeldahl		AutoAnalyzer		Kjeltec	
	meq 100 g^{-1}					
1	14.3	0.67 (4.7)	14.1	0.97 (6.9)	14.2	0.48 (3.3)
2	123	3.33 (2.7)	123	7.72 (6.3)	124	4.85 (3.9)
3	32.9	1.13 (3.4)	32.5	0.97 (3.0)	32.3	0.92 (2.9)
4	9.73	0.18 (1.9)	9.39	0.22 (2.3)	9.60	0.32 (3.4)
5	36.0	0.22 (0.6)	38.4	1.11 (2.9)	37.1	1.34 (3.6)
6	18.0	0.40 (2.2)	18.0	0.23 (1.3)	18.1	0.52 (2.9)
7	22.4	0.16 (0.7)	22.5	0.23 (1.0)	22.1	0.09 (0.4)
8	29.3	1.29 (4.4)	29.8	1.24 (4.2)	29.6	1.11 (3.8)
9	19.4	0.29 (1.5)	19.2	0.59 (3.1)	19.5	0.19 (1.0)
10	20.9	0.40 (1.9)	20.7	0.59 (2.8)	21.0	0.48 (2.3)
11	13.2	0.63 (4.8)	12.9	0.22 (1.7)	13.1	0.63 (4.8)
12	2.36	0.23 (9.6)	2.62	0.21 (7.9)	2.52	0.43 (17.1)
13	8.84	0.31 (3.5)	8.62	0.59 (6.9)	8.76	0.28 (3.2)
14	77.3	6.80 (8.8)	76.8	0.66 (0.9)	73.8	3.18 (4.3)
15	16.0	0.15 (0.9)	15.4	0.67 (4.3)	15.9	0.24 (1.5)
16	1.24	0.26 (21.2)	1.55	0.42 (26.8)	1.21	0.09 (7.1)
17	9.60	0.31 (3.2)	9.26	0.39 (4.2)	9.48	0.18 (1.9)
18	10.6	1.36 (12.7)	10.2	1.78 (17.6)	10.6	1.03 (9.8)
19	61.9	1.07 (1.7)	62.3	2.41 (3.9)	61.3	1.01 (1.6)
20	23.8	1.04 (4.4)	23.1	0.66 (2.9)	23.7	1.18 (5.0)

* All results are the average of three replicates.

** meq 100 g^{-1} = cmol kg^{-1}.

Table 4. Two-way analysis of variance (SAS Institute Inc. 1985)

Source	DF	ANOVA SS	F Value	Significance
Sample.Treatment	38	34.55720111	0.30	NS*
Sample	19	146061.01591722	2496.14	...**
Treatment	2	1.33848778	0.22	NS

Means with the same letter are not significantly different.

SNK#	Grouping	Mean	N	Treatment
	A	27.5567	60	1
	A	27.5397	60	2
	A	27.3658	60	3

* Not significant
** P<0.001
\# Student-Newman-Keuls test for variable.

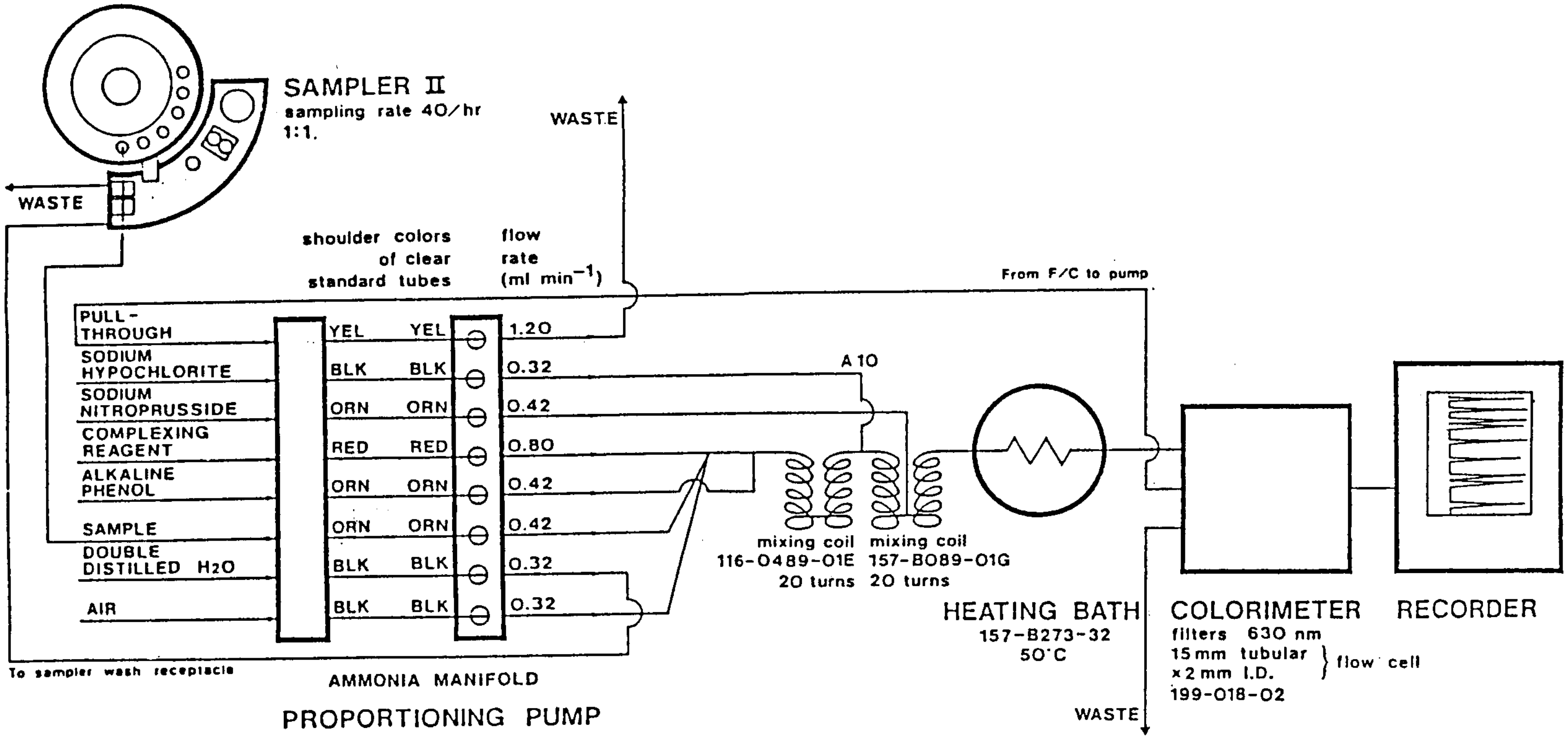

Figure 1. Flow diagram for the determination of NH_4-N in NaCl leachates by AutoAnalyzer

EXCHANGEABLE CATIONS - AN AUSTRALIAN EXPERIENCE

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I Introduction

In recent years in Australia there has been a renewed interest in the determination of Exchangeable Cations and Cation Exchange Capacity (CEC), partly through the wider use of Soil Taxonomy. Australia has an extreme range of soil types from highly leached tropical soils through arid and semi-arid desert soils to heavy clay soils. The range of soluble salts may vary from less than 5 to more than 2000 mg/kg. Carbonate may be present and can constitute as much as 80% of some soils, particularly in the southern states. Consequently several methods are currently in common use in Australia, each found to be suitable for particular soil types. For example, the Compulsive Exchange method using unbuffered $BaCl_2$ is used on the highly leached Oxic soils of Queensland, while a pH 8.5 NH_4Cl extract is used for the predominantly alkaline soils of south Australia.

In this paper some results are presented from a recent study involving a comparison of a number of extractants with a new extractant - Choline chloride - proposed in Australia by Tucker (Tucker, 1985a and 1985b).

Choline chloride is a quaternary ammonium salt with the formula $(OHC_2H_4)(CH_3)_3NCl$ soluble in both water and alcohol to give a neutral solution. For this study we used a 1M solution in 30% water 70 % ethanol (by volume). All the extractions were carried out using the USDA syringe extractors (Holmgren et al., 1977). Soils were extracted with choline chloride in exactly the same way as with the other extractants, with the cations determined on the extract. A second soil sample is required for the CEC determination by first saturating with 0.25 M $CaCl_2$, washing out the excess with alcohol, then extracting with choline chloride. CEC was then estimated by measuring the Ca in the extract.

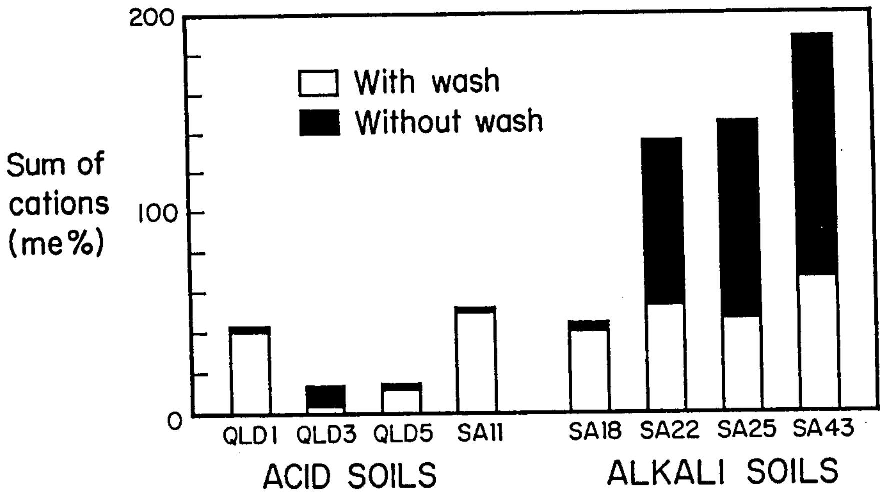
The 5 conventional extractants used were NH_4Cl pH 7.0 (Soil Survey Staff, 1982), alcoholic NH_4Cl pH 8.5 (Tucker, 1974), NH_4OAc, NH_4OAc pH 7.0 (Soil Survey Staff, 1982) and AgThioUrea (AgTU) (Chhabra et al., 1975).

The soils used were leached tropical oxic soils from Queensland (QLD), acid and alkaline soils from South Australia (SA), and the Labex samples 11, 15, 18, 23 and 28.

II Prewashing

In Adelaide we have adopted a procedure of prewashing soils with 70 % ethanol prior to extraction. The leachate may be checked by conductivity for soil with a high concentration of soluble salts (see Figure 1).

Figure 1. Effect of Prewashing when using NH_4Oac pH7



The actual data is given in Table 1. Here we see that even acidic soils can have appreciable quantities of salts although this is not general. Results on the other acidic soils show no difference between the prewashed and the untreated samples. The saline and calcareous soils however show large differences between treatments. These differences could not all be accounted for by calculation from the salt content in the saturation extracts, particularly if gypsum was present. We believe that you either preferably wash out the soluble salts or determine them in an extract obtained with the same soil/extractant ratio as used in the exchangeable cation determination.

III Comparison of Extracts - Acid Soils

Figure 2 is a bar graph showing the four measured exchangeable cations using six extractants on acid soils. In this and following bargraphs the first row of the legend corresponds to the left-most three bars and the second row of the legend to the right-most three bars of each group of six. You can see that there is little difference between extractants for Na and Mg. Two points here to note are: (a) although Ca does not vary much it is always lower in the NH_4Cl pH 8.5 extract; and (b) K is significantly lower in the choline chloride extract. Both points will be discussed later.

Figure 2. Comparison of Extracts on Exchange Cations ACID SOILS

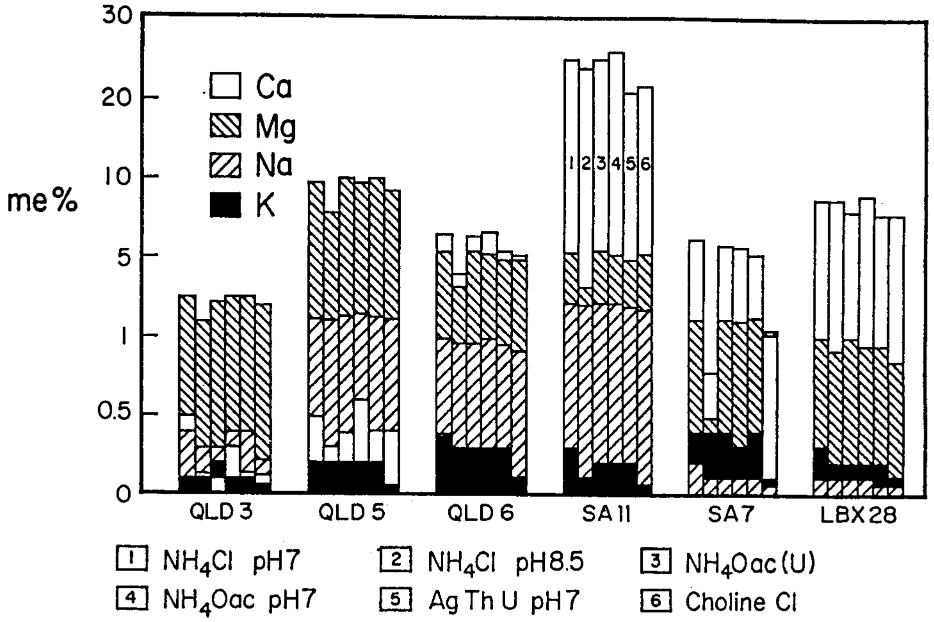
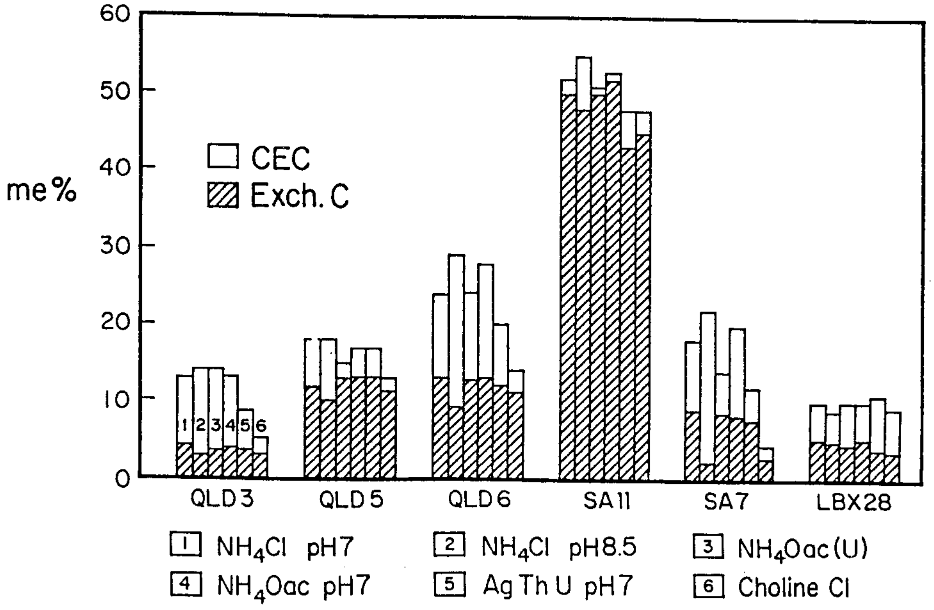


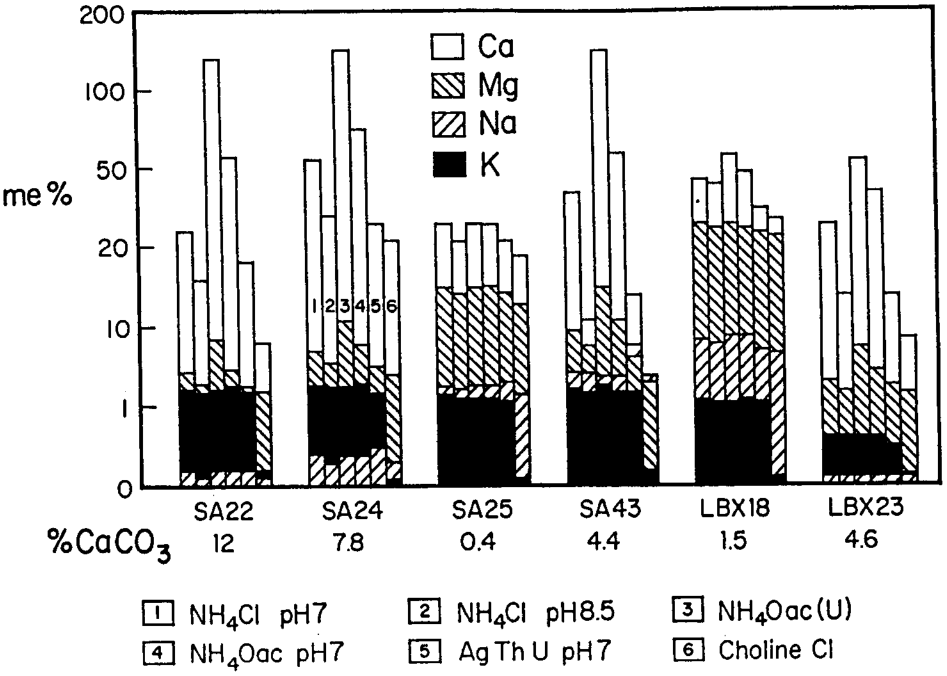
Figure 3 shows the comparisons of the measured CEC and the summation of cations (Exch. C). It is quite clear that there is again a good agreement between all methods although choline chloride was slightly lower for CEC but agrees well with the summations. This data is shown in the upper part of Tables 2, 3 and 4.

Figure 3. Comparison of Extracts on Exch.C and C.E.C. ACID SOILS



IV Comparison of Extracts - Alkali Soils

Figure 4. Comparison of Extracts on Exchange Cations ALKALI SOILS



A different picture is observed with calcareous soils. Figure 4 shows the four measured exchangeable cations using the same six extractants. Here once again there is good agreement between the results for both Na and Mg and also lower K results in the choline chloride extractant as observed with the acid soils. Ca however shows the now well known variation, particularly note the very large differences between the acetate extracts unadjusted and adjusted to pH 7 (bar graphs 3 and 4). This indicates that great care must be taken to ensure that this reagent is in fact adjusted precisely to pH 7 prior to use. Choline chloride provides the lowest Ca values followed by NH_4Cl pH 8.5 then AgTU.

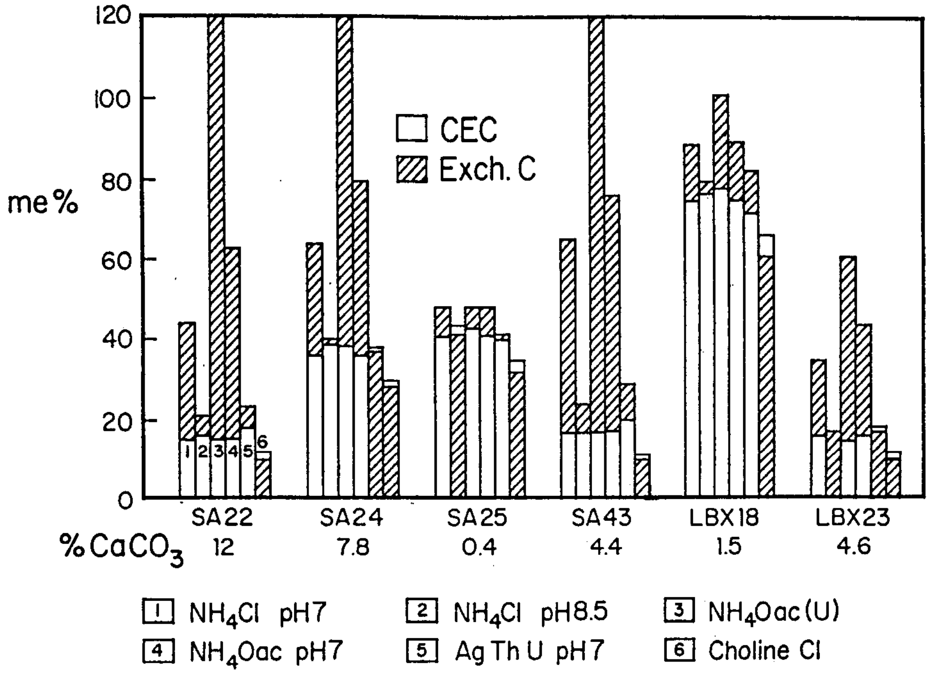
K for example in Illitic clays is known to be specifically adsorbed. However, both NH_4^+ and H^+ ions will displace some of it from the interlayers. This may be the reason for the higher K values in all the extractants containing NH_4^+. The lower K values of choline chloride may be closer to the "real" exchangeable value.

Figure 5 shows the comparison between CEC and exchangeable cations and it is immediately obvious that only choline chloride and NH_4Cl pH 8.5 balance the summation with that of the CEC. Again the CEC shows good agreement between all methods. This data is shown in the lower part of Tables 2, 3 and 4.

NH_4Cl pH 8.5 is not as suitable as these results would indicate. It is a buffered solution far removed from many of the soil pH's (see section III). Also the higher pH increases the negative charge on the surface of the soil particles to such an extent that Ca will be more strongly adsorbed. Hence as indicated in section III with non calcareous soils the Ca results were significantly lower with NH_4Cl pH 8.5 relative to the other, more acidic ammonium salt solutions.

Our limited experience with the AgTU reagent shows that it is not as good for calcareous soils as choline chloride but in most cases better than the other. We did find that prior knowledge of expected CEC values was necessary so that an adequate volume of AgTU was used.

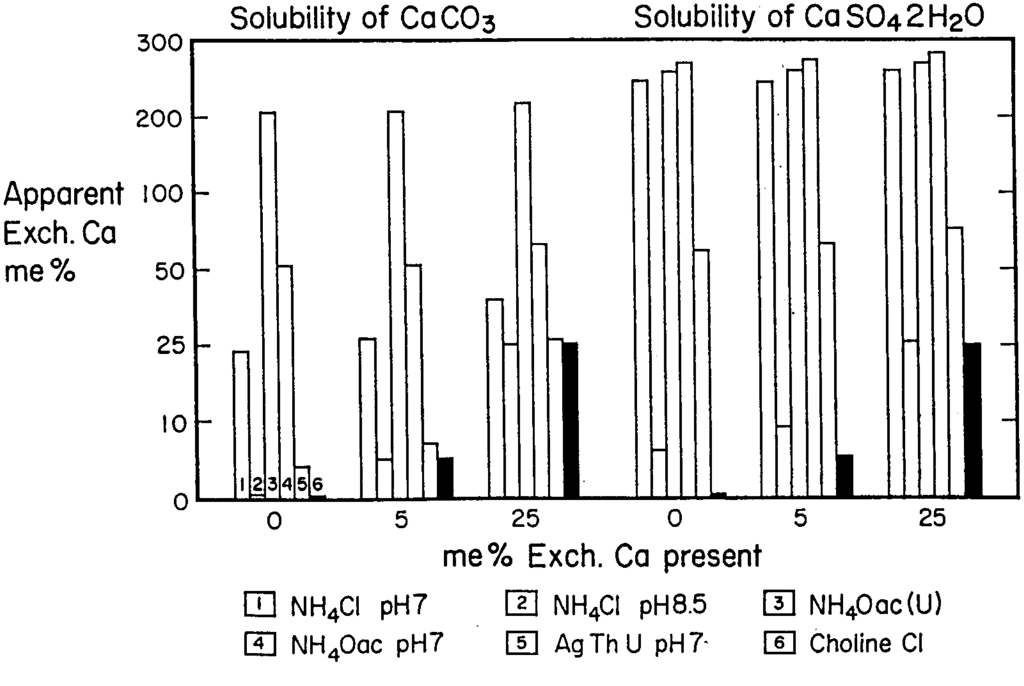
Figure 5. Comparison of Extracts on Exch.C and C.E.C.
ALKALI SOILS



V The solubility of Ca from Carbonate and Gypsum

We carried out a very simple experiment to determine the solubility of Ca from both gypsum and $CaCO_3$ in all the extractants used in this study.

Figure 6. Solubility of Ca from Carbonate and Gypsum



Aliquots of $CaCO_3$ and $CaSO_4.2H_2O$ were extracted in triplicate with each extractant, and Ca was determined in the leachates. From the mean Ca values the solubility product was determined. From this was calculated the apparent exchangeable Ca which would be determined from soil containing 0, 5 and 25 meq/100 g exchangeable Ca as well as excess $CaCO_3$ or gypsum (Table 5).

Figure 6 shows the results and it is interesting to note that no Ca was dissolved from $CaCO_3$ or $CaSO_4.2H_2O$ by the choline chloride.
AgTU did not dissolve Ca from $CaCO_3$ but did precipitate Ag which would lead to overestimations of CEC. This reagent did however dissolve Ca from $CaSO_4.2H_2O$. Again NH_4Cl ph 8.5 did not dissolve Ca from $CaCO_3$ for the reasons previously discussed. These results help to explain an anomaly which occured with two Labex soils both containing the same amount of carbonate:

	pH	Clay %	CO_3 %	Exchangeable Ca using Extractant NH_4Cl	 NH_4OAc (Ca meq/100 g)	 Choline Cl
Lbx 11	8.0	34	24	106	108	12
Lbx 15	10.5	19	24	34	56	9.6

These Ca values show that there was a very large difference between the two soils. From the carbonate solubility Lbx 11 should produce the same apparent exchangeable Ca as the other. If however this soil also contained gypsum then more Ca would be dissolved from $CaSO_42H_2O$ by both NH_4Cl and NH_4OAc than from just $CaCO_3$. Further investigation showed that Lbx 11 did in fact contain gypsum.

VI Conclusion

No specific recommendation of any one method for Exchangeable Cations is made. This report indicates clearly that soluble salts must be washed out before extraction (the USDA method of correction from the results of saturation extracts requires additional analyses and is not valid with gypseous and calcareous soils). Unbuffered extracts should be used as large errors can occur when determinations are made at pH values far removed from the natural soil solution pH. The data also indicates that no single NH_4Cl or NH_4OAc extractant is suitable for all soils; several methods would be necessary to span a range of soil pH. It would be preferable if an extractant could be chosen which is suitable for all soil types. One of the proposed new methods using choline chloride is extremely promising and should be given due attention.

In conclusion we believe that choline chloride has great potential as a universal extractant but it must be tested on as large a range of soils as possible to determine its limitations. We would like this to be done through the Labex programme so that it may be assessed internationally over a relatively short period of time.

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TABLE 1 THE EFFECT OF PREWASHING

Sample No	pH	%Clay	%$CaCO_3$	EXCHANGEABLE CATIONS in me/100g					
				Without Prewashing			With Prewashing		
				NH_4Cl pH 7	NH_4Oac pH 7	NH_4Cl pH8.5	NH_4Cl pH 7	NH_4Oac pH 7	NH_4Cl pH8.5
QLD 1	6.9	34		42	42	37	35	39	33
QLD 3	5.8	65		13	14	13	4	4	2
QLD 5	5.6	36		14	14	13	12	12	10
SA 11	7.0	83			52		48	50	48
SA 18	8.5	45	<0.1		44		38	41	36
SA 22	8.5	18	12		135		36	54	18
SA 25	8.1	57	0.4		145		41	46	40
SA 43	8.8	13	4.4		188		47	65	23

TABLE 2 EFFECT OF EXTRACTANTS ON C.E.C. AND SUM OF EX.CATIONS (me/100g)

Sample No	pH	%Clay	%$CaCO_3$	NH_4Cl pH7.0	NH_4Cl pH8.5	NH_4Oac	NH_4Oac pH7.0	Ag Thio Urea	Choline Cl
QLD 3	5.8	65		11	14	14	18	8.3	5.0
				3.5	2.3	3.4	3.6	3.5	3.0
QLD 5	5.6	36		19	18	15	20	17	13
				12	10	13	12	13	11
QLD 6	5.6	49		23	29	24	25	20	14
				13	8.7	13	13	12	11
SA 11	7.0	83		55	55	50	58	48	48
				50	48	51	51	43	45
SA 7	5.8	50		13	22	14	20	12	4.4
				8.4	2.0	8.3	7.9	7.5	2.6
LBX 28	6.9	19		11	8.5	10	8.6	11	8.8
				10	9.6	9.2	9.5	8.8	8.3
SA 22	8.5	18	12	15	16	15	16	18	12
				38	21	152	55	23	10
SA 24	8.3	37	7.8	35	38	38	39	38	30
				55	39	164	70	37	28
SA 25	8.1	57	0.4	41	44	43	42	40	35
				43	41	48	45	41	32
SA 43	8.8	13	4.4	16	17	17	16	20	11
				47	24	170	65	29	10
LBX 18	8.7	84	1.5	85	77	78	78	83	66
				86	80	101	91	72	61
LBX 23	8.1	27	4.6	16	17	15	16	18	12
				28	17	61	39	17	10

Note: For each sample the top row is the C.E.C. data and the bottom row is the sum of ex.cations data

TABLE 3 EXCHANGEABLE CALCIUM AND POTASSIUM (me/100g)

Sample No	pH	Clay %	CaCO3 %	NH4Cl pH7.0	NH4Cl pH8.5	NH4Oac	NH4Oac pH7.0	Ag Thio Urea	Choline Cl
QLD 3	5.8	65		0.26	<0.1	0.10	0.22	0.1	0.12
				0.14	0.12	0.15	0.14	0.12	<.05
QLD 5	5.6	36		0.45	0.28	0.42	0.46	0.39	0.37
				0.19	0.15	0.17	0.19	0.18	<.05
QLD 6	5.6	49		6.1	3.8	6.4	6.8	5.7	5.4
				0.32	0.31	0.31	0.31	0.30	0.05
SA 11	7.0	83		25	24	25	25	21	22
				0.24	0.14	0.17	0.18	0.18	<.05
SA 7	5.8	68		5.8	1.1	5.9	5.6	5.1	1.2
				0.39	0.37	0.36	0.38	0.37	0.10
LBX 28	6.9	19		8.5	8.6	8.0	8.2	7.6	7.5
				0.24	0.17	0.18	0.22	0.23	0.05
SA 22	8.5	18	12	32	16	140	48	18	8.0
				2.3	2.2	2.2	2.2	2.1	0.22
SA 24	8.3	37	7.8	46	31	150	60	30	24
				2.1	2.1	2.1	2.2	1.8	0.07
SA 25	8.1	57	0.4	26	24	30	27	23	19
				1.4	1.5	1.5	1.5	1.3	<.05
SA 43	8.8	13	4.4	33	11	150	49	14	3.1
				1.7	1.6	1.8	1.7	1.7	0.15
LBX 18	8.7	84	1.5	46	42	58	47	37	30
				1.2	1.1	1.1	1.2	1.1	<.05
LBX 23	8.1	27	4.6	24	14	53	34	14	8.5
				0.68	0.59	0.60	0.72	0.48	<.05

Note: For each sample the top row is the calcium data and the bottom row is the potassium data

TABLE 4 EXCHANGEABLE MAGNESIUM AND SODIUM (me/100g)

Sample No	pH	Clay %	$CaCO_3$ %	NH_4Cl pH7.0	NH_4Cl pH8.5	NH_4Oac	NH_4Oac pH7.0	Ag Thio Urea	Choline Cl
QLD 3	5.8	65		2.9	1.8	2.8	2.9	2.9	2.6
				0.28	0.26	0.34	0.38	0.37	0.22
QLD 5	5.6	36		9.4	7.8	10	9.7	10	9.1
				2.0	2.0	2.0	2.0	2.2	1.9
QLD 6	5.6	49		5.4	3.7	5.5	5.2	5.0	5.1
				0.89	0.86	0.91	0.92	0.94	0.80
SA 11	7.0	83		22	21	23	23	19	21
				2.6	2.6	2.6	2.5	2.6	2.1
SA 7	5.6	50		2.1	0.48	1.9	1.8	1.9	1.3
				0.12	0.09	0.13	0.11	0.13	<.05
LBX 28	6.9	19		0.99	0.76	0.98	0.97	0.92	0.70
				0.09	0.05	0.05	0.14	<.05	<.05
SA 22	8.5	18	12	3.7	2.7	9.2	4.4	2.9	1.9
				0.12	0.07	0.23	0.16	0.18	0.07
SA 24	8.3	37	7.8	6.4	5.3	11	7.4	5.0	4.0
				0.28	0.30	0.37	0.42	0.45	0.25
SA 25	8.1	57	0.4	14	14	15	15	14	12
				1.9	1.7	1.8	1.7	2.6	1.4
SA 43	8.8	13	4.4	8.8	7.5	15	10	6.0	3.4
				3.8	4.1	3.9	4.1	7.4	3.8
LBX 18	8.7	84	1.5	31	29	33	33	27	24
				8.0	7.8	9.3	9.4	7.0	6.8
LBX 23	8.1	27	4.6	3.3	2.4	7.4	3.8	2.5	1.9
				0.08	0.06	0.10	0.14	0.05	0.06

Note: For each sample the top row is the magnesium data and the bottom row is the sodium data

TABLE 5 SOLUBILITY OF Ca FROM $CaCO_3$ & $CaSO_4.2H_2O$

		$CaCO_3$					$CaSO_4.2H_2O$				
		Ca	Ksp	I-----	me% Ex.	-----I	Ca	Ksp	I----	me% Ex.	-----I
Reagent	pH	mg/l	$\times 10^8$	0	5	25	mg/l	$\times 10^6$	0	5	25
NH_4Cl	7.0	242	3650	24.2	26.8	39.7	2447	3741	245	247	257
alc NH_4Cl	8.5	0.40	0.010	0.04	5.00	25.0	62	2.39	6.19	9.18	26.4
NH_4OAc	6.1	2060	265200	206	209	219	2573	4139	257	260	270
NH_4OAc	7.0	519	16810	51.9	54.4	65.8	2700	4556	270	273	283
AgThU	7.0	39	93.8	3.87	7.11	25.6	633	251	63.3	65.9	77.1
CholineCl	6.8	0.27	0.004	0.03	5.00	25.0	4.47	0.012	0.45	5.04	25.0

Note: Ksp is the solubility product, the product of the concentrations of the calcium cation and the carbonate or sulfate anion in moles per litre in a saturated solution.

COMPARISON OF EXCHANGEABLE BASES AND CEC BY THE COBALTI-HEXAMMINE METHOD AND THE STANDARD AMMONIUM ACETATE METHOD ON SOME MALINESE SOILS

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I Introduction

For many soil-laboratories the cation exchange capacity of a soil (CEC) and the exchangeable bases are frequently requested parameters. They are used to understand the soil's behaviour with respect to various fertilization practices, as well as to study salinization problems. Furthermore, in soil taxonomy the CEC and % base saturation are used to distinguish between the alfisols, ultisols and oxisols.

Various methods have been applied to measure CEC and exchangeable bases, the most well-known being the percolation method with 1M ammonium acetate at pH=7. This method is laborious, and since the CEC of a soil varies with the pH at which the soil is buffered, the values measured at pH=7 tend to overestimate the actual cation exchange capacity of the more acid soils. These disadvantages can be avoided by using metal-ligands, some of which appear to be very strongly adsorbed by the soils exchange complex. The ligands allow determinations at soil-pH, while the low concentration needed to saturate the soil with the ligand permits a rapid CEC-determination by difference, together with the exchangeable bases in the same extract.

Pleysier (1973 and later) worked with the strongly adsorbed silver thioureum ligand, whereas Orsini and Remy (1976) proposed cobalti-hexammine chloride as exchanger. Some problems with the low stability of the silver thiourea ligand have been experienced (Van Rosmalen, 1979), resulting in deterioration of the extraction solution, and breakdown of the ligand in soils with high pH. In this respect the cobalti-hexammine ligand seems to offer better possibilities.

Oliver (1984) compared the cobalti-hexammine method with the traditional ammonium acetate-percolation method for soils from Senegal, and he found good correlations for the exchangeable bases, and fair correlations between the CEC values obtained. Recently Fallavier et al. (1985) compared the results of various CEC methods with theoretically derived values for soils from the humid tropics. CEC values by cobalti-hexammine were found to correspond better with the theoretical values than those obtained by most other methods. In this paper we will compare the results of the cobalti-hexammine method and of the classical ammonium-acetate percolation method for some soils from Mali.

II Materials and methods

1. Soils

Eleven soils from Mali have been selected representing various conditions in Mali. Some important characteristics of these soils are compiled in Table 1. All soils have been sampled at two depths: 0-20 cm and 20-40 cm.

2. Methods

The soils have been analyzed:

- At the Soils Laboratory of the Institute of Rural Economy (IER), Sotuba, by the classical percolation method with neutral ammonium-acetate: 5 g soil is mixed with 10 g purified sand and transferred in a percolation tube. The soil is percolated with 100 ml 1M ammonium acetate at pH 7. In the leachate Ca and Mg are determined by atomic-absorption-spectrometry, and Na and K by flame-spectrometry. Then the soil is washed with 150 ml ethanol 96%, or more, until reaction with Nessler's reagent is negative. The absorbed ammonium is liberated by percolation with 100 ml of an acidified sodiumchloride solution (10% NaCl + 0.005 N HCl), and determined by autoanalyzer.
- At the soils laboratory of the International Centre for Agricultural Research and Development (CIRAD), Montpellier, by the cobalti-hexammine method: 4 g of soil is transferred in a 100 ml centrifugation tube and 80 ml of $Co(NH_3)_6\ Cl_3$ solution is added. The Co-concentration in meq/l should be between 1 and 2.5 times the expected CEC value in meq/100 gr After 2 hours extraction on a rotating agitator, the soil suspension is centrifugated and Co and the exchangeable bases are determined by atomic absorption spectrometry.

III **Results and discussion**

1. Influence of depth of sampling

In order to establish whether soils sampled at both depths can be treated as one set, a test is carried out on the influence of soil depth on the relation between the two analytical methods. The mean differences between the values that both methods produce for the sum of bases and the cation exchange capacity are compared in Table 2. It may be concluded that soil depth is not an important parameter when treating differences in results obtained by the two methods. Therefore, in the following discussions samples from both depths will be treated as belonging to one and the same set.

2. Exchangeable bases

The relations between the results obtained by the two methods for the exchangeable bases Ca, Mg, Na and K are presented in Fig. 1a, b, c, and d. Those for the sum of bases and CEC in Fig. 2 and 3. In Table 3 some statistical data pertaining to these figures are presented.

A good relation appears to exist for Ca and Mg. Scatter for K and Na is somewhat higher, which also has been reported by Oliver (1984). This will be due to analytical errors, as the standard error of estimate is low: 0.03 meq/100 g soil, which is of the order to be expected for this method. The sum of bases mainly reflects the good relationships obtained for Ca and Mg.

Although results for Ca and Mg as found by both methods are highly correlated, the cobalti-hexammine method appears to extract 10-20% more than the ammonium acetate percolation method. This is not consistent with the results of Oliver (1984), who reports equal or lower results by the cobalti-hexammine method, but it is in accordance with the work of Fallavier et al. (1985). It is quite well possible that those anomalies are caused by differences in the results of the classical ammonium-acetate method, since the Labex international exchange scheme reports minimal differences of ±10% between laboratories. (Van Reeuwijk, 1984).

3. Cation exchange capacity

The CEC values as resulting from both methods are in good agreement, but the standard error of estimate is larger than can be expected from an analytical point of view. This means that the various soils behave differently with respect to both methods, as has also been reported by Oliver (1984) and Fallavier et al. (1985). The lower values obtained by the cobalti-hexammine method is in agreement with the findings of these authors.

We have tried to explain the differences between both methods by factors as soil pH, organic matter content and clay content, but correlation with these factors is very low (less than 0.3). By including pH and clay content in a multiple regression test, only a slight improvement was obtained (see Table 3 and Fig. 5). The resulting error is still larger than can be expected on analytical grounds.

IV Conclusions

The present study shows the existence of a good relationship between the values of exchangeable bases obtained by the cobalti-hexammine method and the traditional percolation with neutral ammonium acetate. Differences are of the same order of magnitude as are inter-laboratory variations for a single method.

CEC values produced by the cobalti-hexammine method are in most cases lower than those produced by the percolation method. The differences can be explained only partly by the factors pH, organic matter content, and clay content. This means that for conditions in Mali conversions between values from both methods should be done with care. The best fitting relation for the studied set of data is CEC Co-hexammine = 0.53 x CEC NH_4OAc + 0.97 x pH + 0.41 %clay - 5.83. From an analytical point of view the cobalti-hexammine method offers a more straightforward way of analyzing, and therefore could be less subject to manipulation errors.

V Acknowledgement

The authors wish to acknowledge the staff of the laboratory of CIRAD, Montpellier and IER, Bamako, for their kind cooperation and Ir. Martinez from the IER for making the soil samples available.

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Table 1 - Characteristics of the tested soils

Soil nr	location	description and cultures	pH (KCl)	%Clay	%Org.Mat
1a	Koporo	sandy "ferruginous"soils,	5.4	3	.4
b		plains with ancien dunes/millet	4.7	6	.3
2a	Cinzana	sandy "ferruginous" soil	4.7	6	.5
b		millet, limit for cotton	4.2	10	.6
3a	Samanko	loamy "leached ferruginous"	4.5	15	1.1
b		soil from the river plains/	4.3	26	1.0
		sorghum, maize, groundnuts			
4a	Sotuba	idem, on ancient alluvial	5.0	16	.9
		plains	5.3	22	1.0
5a	Kita	loamy sandy "leached ferruginous" soil with concretions/	5.8	8	1.0
b			5.6	15	1.0
		millet, maize, groundnuts			
6a	Sirabala	soils of the interior Niger	5.5	12	.7
b		delta. Vertisols of alluvial	5.1	16	.6
7a	"	plains associated with sandy	5.6	27	.9
b		dune soils/rice, sugar cane	5.4	33	.7
8a	"		6.0	11	.5
b			5.3	14	.5
9a	Dougabougou	idem, sugar cane	6.3	30	1.0
b			6.1	37	.9
10a	"		6.3	33	1.2
b			6.1	42	.9
11a	"		5.5	30	.5
b			5.0	46	.6

a: depth = 0-20 cm
b: depth = 20-40 cm

Table 2 - Difference by depth

	differences in results for cobalti-hexammine and ammonium acetate percolation method in meq/100 gr.	
	sum of bases	CEC
mean ± st.dev.for:		
0-20 cm	- 1.0 ± 0.6	1.2 ± 1.0
20-40 cm	- 1.0 ± 0.5	1.8 ± 1.1

Table 3 - Relation between results from the cobalti-hexammine and the ammonium acetate percolation methods.

parameter	correlation coefficient	standard error** of estimate meq/100gr	regression coefficient	intercept meq/100gr
Exch. Ca	0.996	0.40	1.15	0.39
Exch. Mg	0.994	0.10	1.09	-0.05
Exch. K	0.897	0.03	1.03	0.01
Exch. Na	0.902	0.03	0.95	0.05
Sum of bases	0.995	0.35	1.13	0.37
CEC	0.962	1.07	0.94	-1.04
LC*	0.979	0.80	1.00	0.00

*) Linear Combination = 0.53 x CEC NH_4OAc + 0.97 x pH + 0.41 x %clay - 5.83

**) Standard error of estimate = $\sqrt{\sum d^2/(n-1)}$ where d is difference between line and point

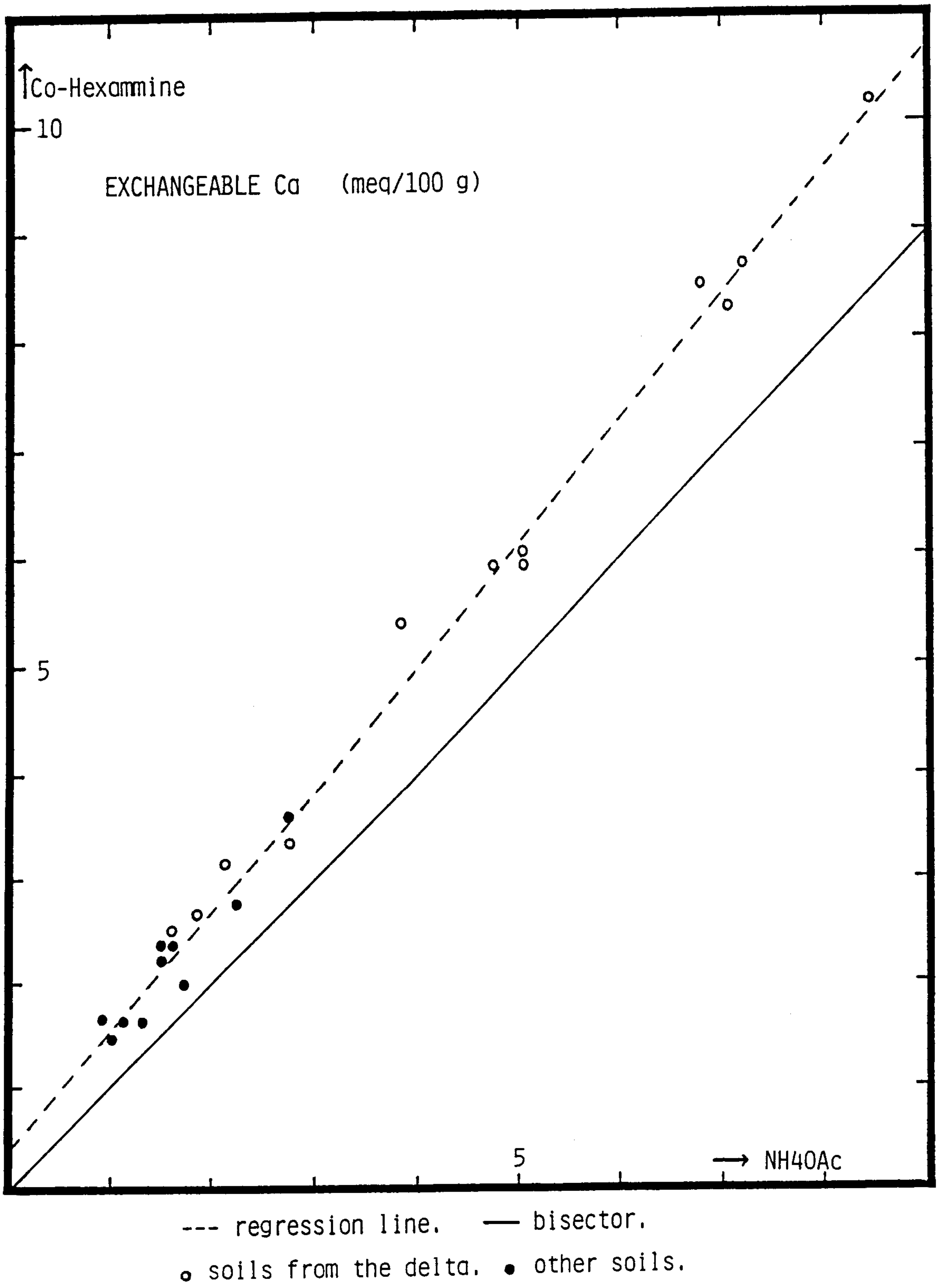


Figure 1a. Comparison of cations exchanged by the classical ammonium-acetate and the cobalti-hexammine method.

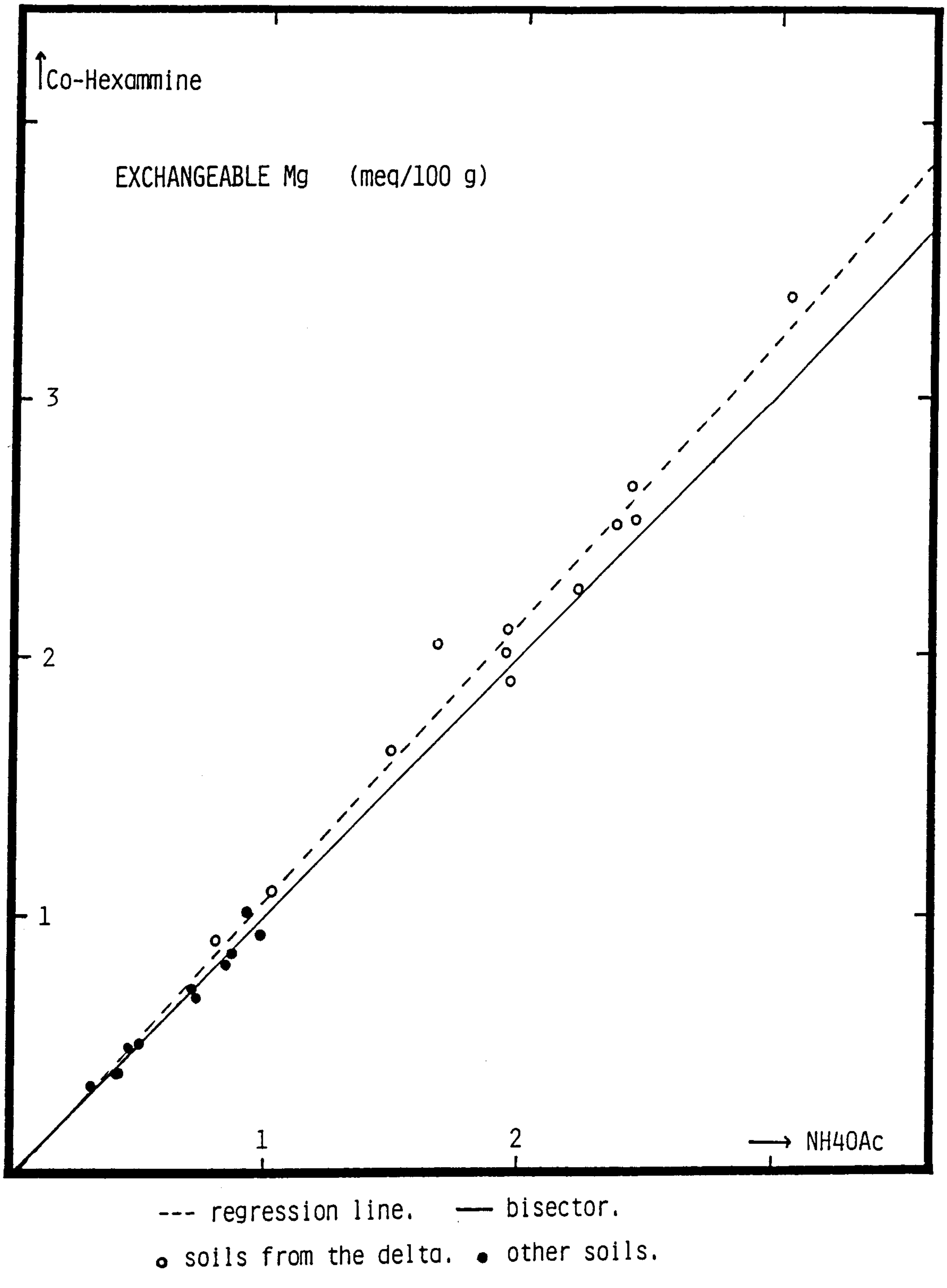


Figure 1b. Comparison of cations exchanged by the classical ammonium-acetate and the cobalti-hexammine method.

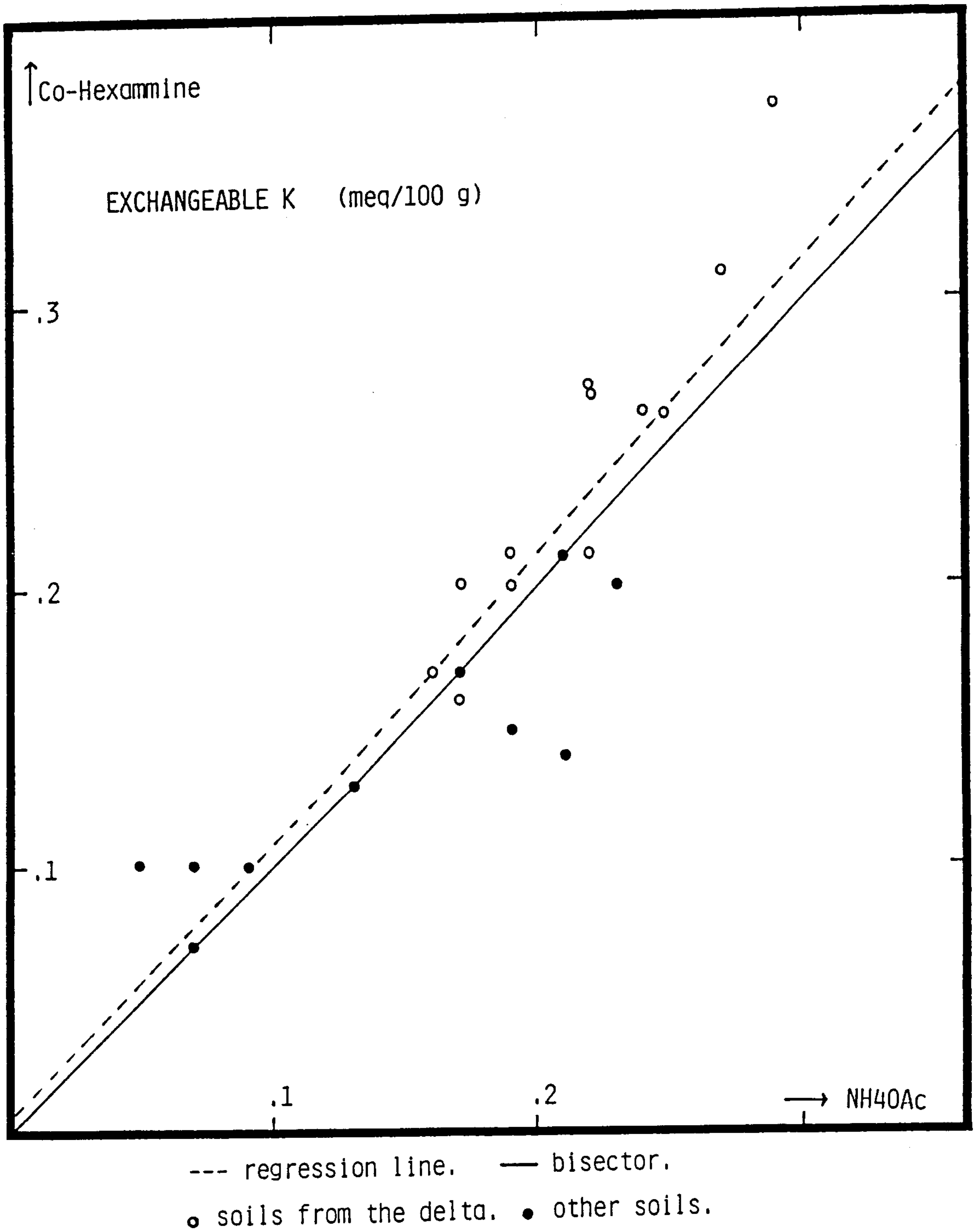


Figure 1c. Comparison of cations exchanged by the classical ammonium-acetate and the cobalti-hexammine method.

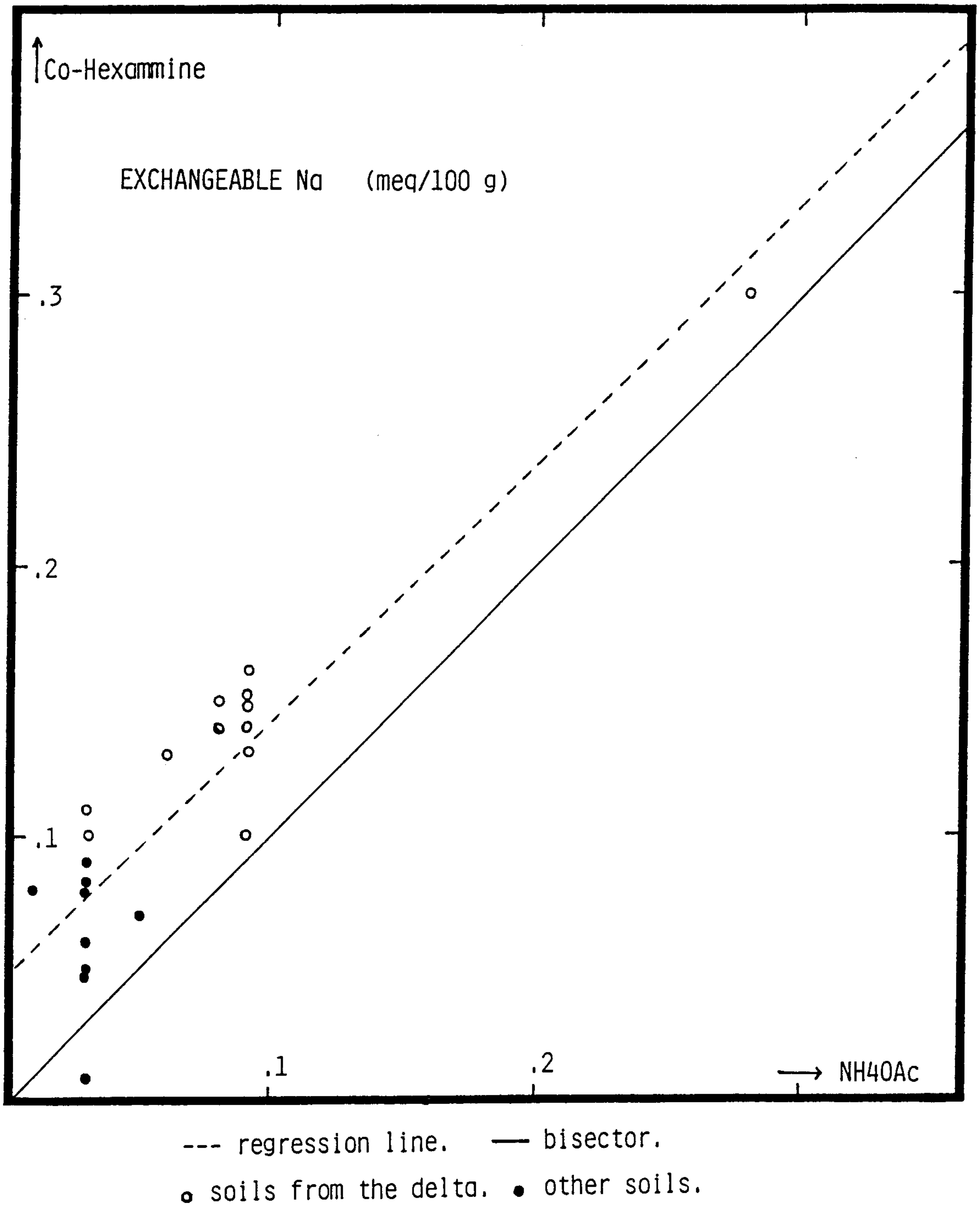


Figure 1d. Comparison of cations exchanged by the classical ammonium-acetate and the cobalti-hexammine method.

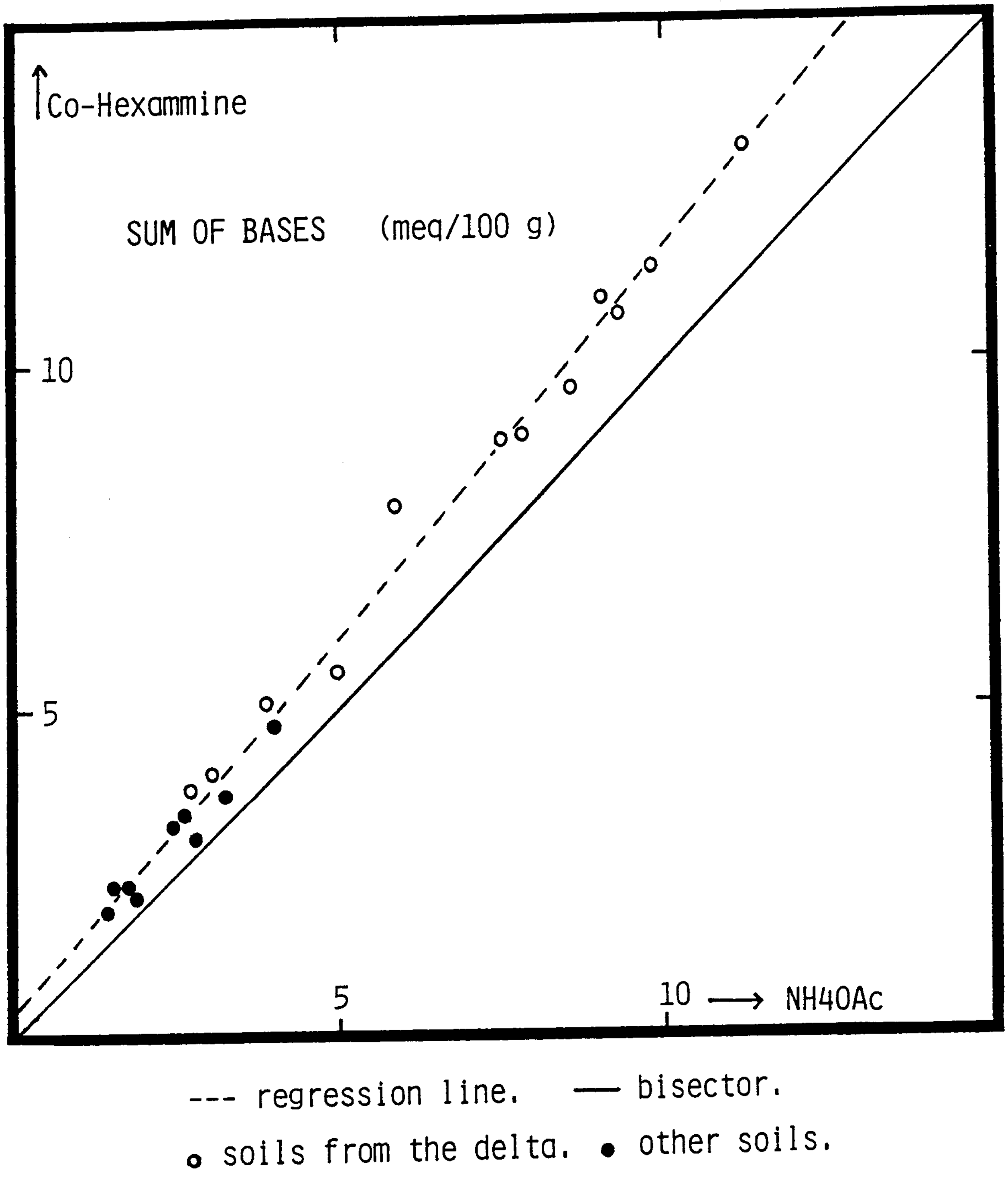


Figure 2. Comparison of the sum of bases by the classical ammonium-acetate method and the cobalti-hexammine method.

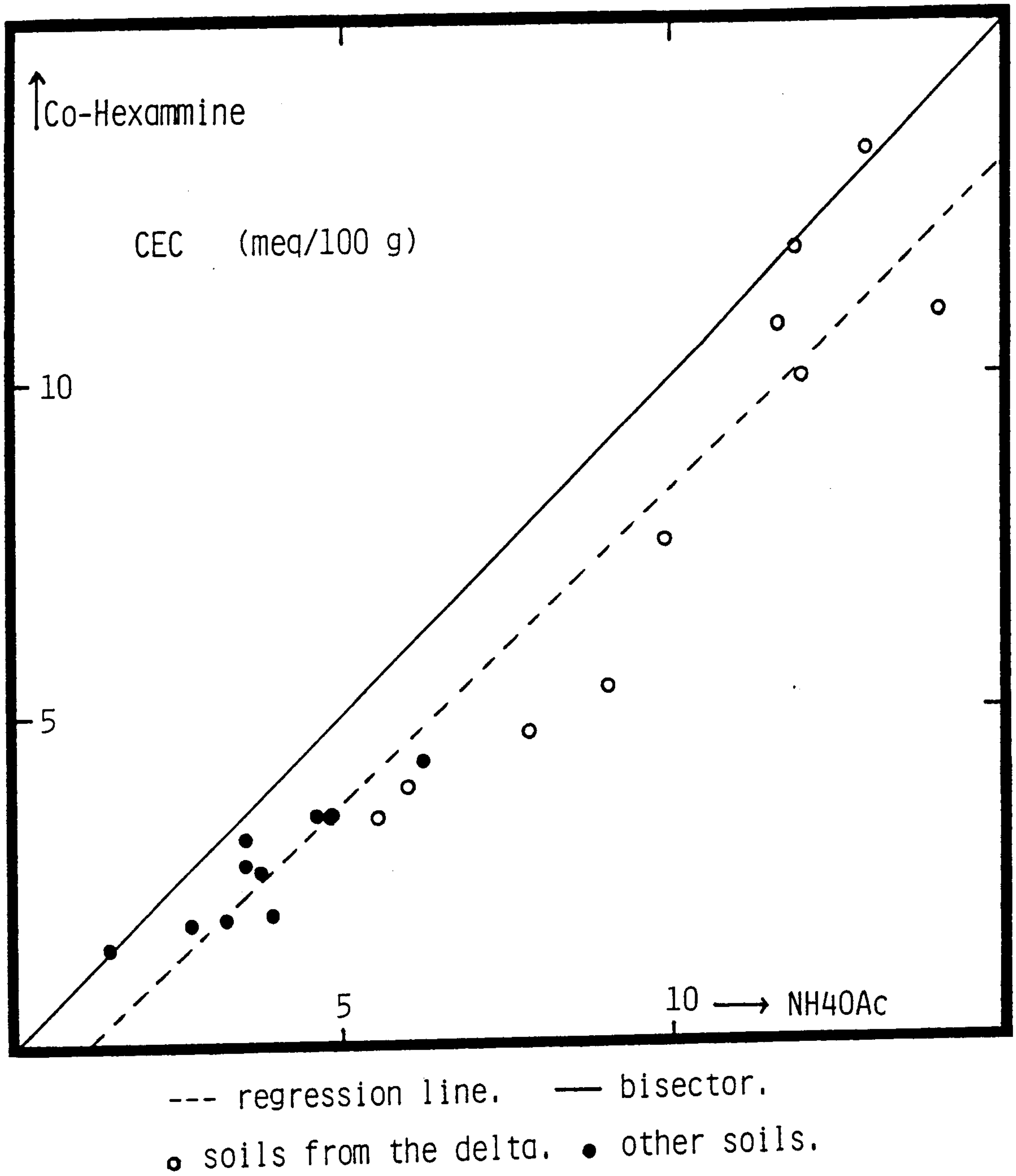
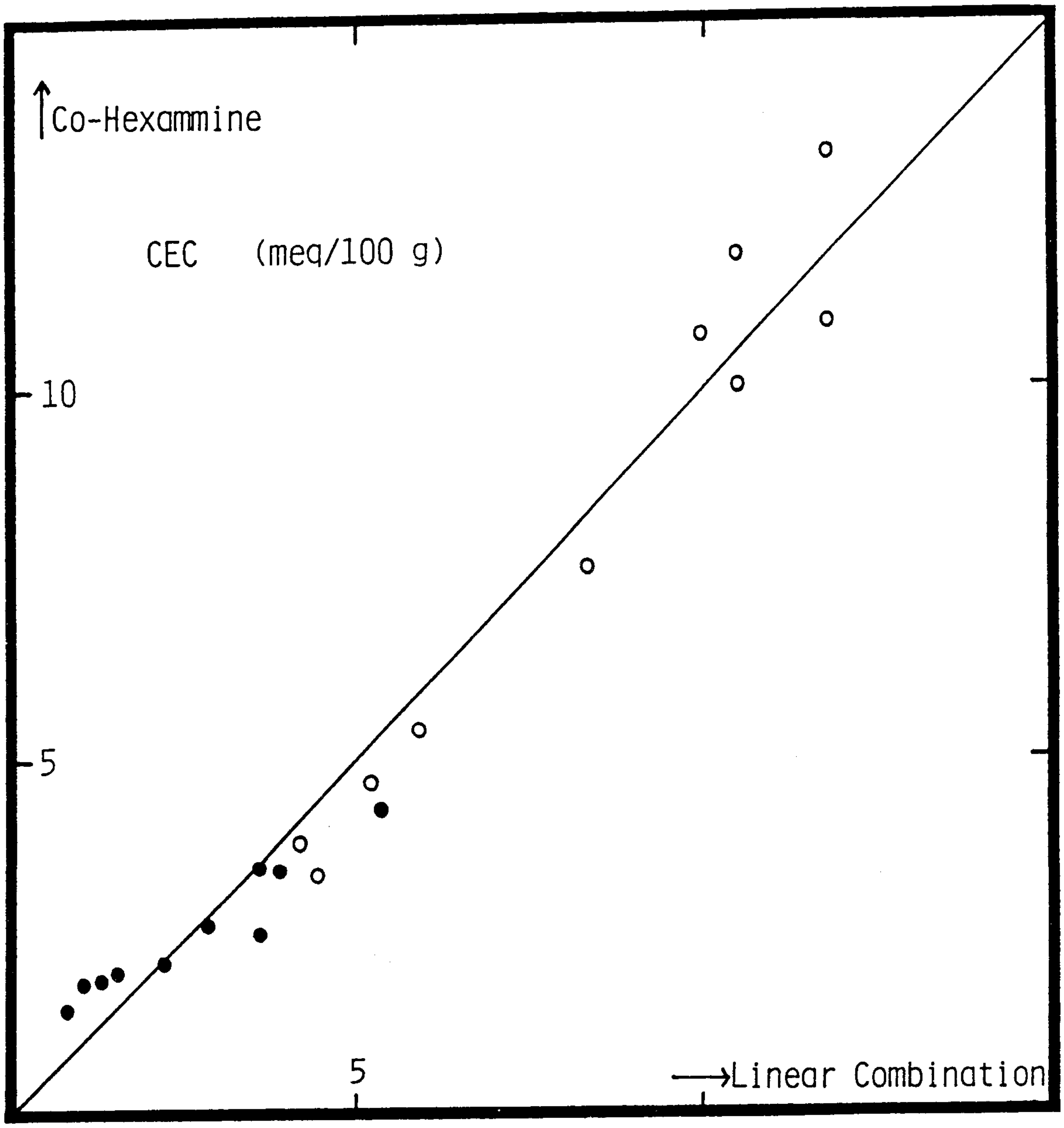


Figure 3. Comparison of CEC values obtained by the classical ammonium-acetate and the cobalti-hexammine method.



--- regression line. —— bisector.

○ soils from the delta. ● other soils.

Figure 4. Best fitting linear combination of the classical ammonium-acetate method, pH and clay-content, compared with CEC values obtained by the cobalti-hexammine method.

DETERMINATION OF CEC AND EXCHANGEABLE CATIONS IN SOILS FROM DIFFERENT CLIMATIC REGIONS USING BARIUMCHLORIDE-TRIETHANOLAMINE AND AMMONIUM ACETATE

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I Introduction

The exchange reactions between the solid and liquid phases of a soil, which occur at the surface of inorganic and organic soil particles, fulfill the following important functions:

- regulate the supply of plants with essential mineral nutrients,
- prevent downward seepage of plant nutrients in periods of high rainfall and low crop demand,
- regulate the soil's capacity to act as a filter for wanted and unwanted substances spread on the ground surface, and
- protect groundwater from contaminated seepage.

Thus a soils capacity to absorb cations and anions on particle surfaces while remaining in equilibrium with the soil solution can be regarded as its most important chemical property.

Potential CEC, base saturation and effective CEC reflect the kind and quantity of clay minerals as well as the content and grade of humification of the organic matter.

Base saturation, e.g. the degree of saturation of a soil's exchange complex with various cations depends on the degree of soil development.
The processes which affect soil development are leaching of divalent cations, migration of clay particles and organic matter in the soil profile, destruction of clay minerals and accumulation of residual iron and aluminium as well as the accumulation of exchangeable sodium or soluble salts.

Thus CEC and exchangeable cations are important parameters in the assessment of a soil's fertility and its suitability for cropping. Modern soil classification systems, such as the FAO/UNESCO Systems or the USDA Soil Taxonomy, use CEC and base saturation for classification at different taxonomic levels.

Accurate determination of CEC and exchangeable cations is therefore of primary importance for the mutual understanding of soil scientists working in different parts of the world.

II Standardization of methods

In the latest issue of the ISSS bulletin under the heading "50 years ago" I discovered an announcement, asking for participation in cooperative work to study the displacement of exchangeable bases by various methods, and to measure the exchangeable bases content of a soil, when saturated.
The announcement was dated February 3rd, 1936 and signed by D.J. Hissink, at that time acting president and Honorary General Secretary of the ISSS.

When studying Peter van Reeuwijks report on the Pilot Round of ISRICs Laboratory methods and Data Exchange Programme, one gets the impression, that during the past 50 years the problem of analytical variability between the various methods and the different laboratories has not been solved, in spite of more sophisticated methods and instruments, which have been introduced. When comparing the methods used for determination of CEC among the 20 participating laboratories, 14 labs used acetate solutions for extraction, but just 5 of them used leaching as the extraction methods, the same pH of the acetate solution and the same method of NH_4- determination. The time that soil and exchanger solution were in contact was never the same for any 2 laboratories.

It is no wonder that the variability amongst the results was tremendous and that standardization of analytical procedures was regarded as a step of the very first priority in the endeavours to reduce it.

During Labex rounds 85-1 and 85-2 the same soil samples were analysed according to
- the methods employed by the participating laboratories in routine analyses (85-1 = x) and
- standardized procedures described in detail by ISRIC (85-2 = y).

Taking into consideration the results of the 30 laboratories for all 15 samples in both rounds mean CEC was 39.5 meq/100 g for the routine methods and 22.82 meq/100 g for the standardized acetate method. The standard deviation for routine methods was 968% and with the standardized method was 176,9%.

There is no correlation between the analyses obtained by the routine methods (x) and those using of the standardized method (Y) when all 900 data are considered, but reducing the data to the means for the 15 samples, there is a close correlation as Fig. 1 demonstrates. Regression line follows

$$Y = -2.465 + 1.1154 \cdot x$$
$$x = 0.9998$$

The coefficient of correlation between routine analysis in round 85-1 and standardized procedure in round 85-2 was over 0.99 for 15 laboratories.

Not knowing the methods these laboratories use for routine analysis, I assume that they use the acetate-method or variations on it.

There were 9 laboratories were the coefficient of correlation between the results of the two rounds varies between 0.91 and 0.98 and just 3 laboratories were the coefficient of correlation was less then 0.70. For the rest it is between 0.71 - 0.90.

It can be concluded that 24 out of 30 laboratories produced closely correlating results for the two rounds. The variability between the results of different laboratories appears to be associated with the assistants' skill and laboratory conditions, rather than a matter of standardizing the procedures in detail.

III Comparison of methods for the assessment of CEC and exchangeable Cations in soils from different climatic regions

For the determination of CEC and exchangeable cations the $BaCl_2$-TEA method suggested by Mehlich (1942) was introduced about 30 years ago as a standard procedure for determining soil-mapping parameters in Lower Saxony. Subsequently the procedure was taken over by the Fed. Inst. f. Geosciences and Natural Resources.

The method proved to be highly reproducible and accurate with post-Pleistocene soils developed under the temperate climatic conditions of Europe and North America. However, procedures suitable for soils developed under temperate climate conditions may not be universally adaptable for soils developed in tropical and subtropical climates.

In particular CEC and exchangeable cations of saline and alkaline soils, containing soluble sulphates, can not be determined reliably using a solution of Ba-salts. For such soils Bouwer, Reitemeier and Fireman (1952) suggested the use of sodium- and ammonium-acetate solutions for assessment of CEC and exchangeable cations.

Soil laboratories in Brazil determine exchangeable Ca and Mg by extraction with unbuffered 1 N KCl-solution and K and Na by 0.05 N HCl + 0.025 N H_2SO_4. CEC is calculated by summation of the data of the four cations determined.
In order to test the comparability of these methods we determined CEC and exchangeable cations using the above mentioned procedures for

- 31 noncalcareous and 2 slightly calcareous samples from the southern part of the copperbelt province of Zambia,
- 34 calcareous and partly saline soil samples from the Conlara valley in Argentine, and
- 40 soil samples from Piaui in Brazil.

3.1 The $BaCl_2$-TEA method - Reproductivity of results

Reproducible results are the first requirement for an analytical method. The 33 soil samples from Zambia were analyzed in spring 1975 and two years later in spring 1977. During the two years the soil samples were stored at normal room temperature (about 20°C) in air dry conditions.

Coefficients of correlation between the results obtained in 1975 and 1977 were for

- CEC	r = 0.9985	t = 1855
- Exchangeable Mg	r = 0.9984	t = 1117,0
- Exchangeable Ca	r = 0.9937	t = 442
- Exchangeable Acidity	r = 0.9799	t = 137

The close correlation between the results obtained in 1975 and 1977 indicates, that the data, produced by percolation with $BaCl_2$-TEA solution adjusted to pH 8.2, are highly reproducible.
The values for CEC and exchangeable Mg are almost equal. There is some variation for exchangeable Ca and exchangeable acidity although it is insignificant. This is explained by a slight deviation in the adjustment of pH of the exchanging solution, in the sensitivity of the AAS used for

determination of Ca and deviation in the velocity of percolation (duration of contact between soil and liquid) through soils which a high clay content and high CEC.

3.2 Comparison of $BaCl_2$-TEA and NH_4 Acetate for determination of CEC

In order to compare the results of the two methods the 33 samples from Zambia as well as the 34 samples from Argentina were analyzed for CEC, exchangeable Ca, Mg, K and Na.

The procedures used were:
Acetate method: The samples were shaken repeatedly with 1 N Na-acetate solution which is adjusted to pH 8.2. After repeating this treatment four times the sample is washed with ethanol until EC of the supernatant liquid is less than 40 mmhos. The adsorbed Na is replaced by treatment with 1 N NH_4-acetate solution adjusted to pH 7.0. The replaced Na is determined in the extract by means of a flame photometer. Exchangeable Cations are then extracted from a second soil sample by NH_4-acetate pH 7.0. The cations contained in the collected extract are determined by flamephotometer or AAS.

$BaCl_2$-TEA-method: 5 g of a soil sample are placed in a filter tube and 2 x 40 ml 0.2 N $BaCl_2$-TEA mixture buffered at pH 8.2 and 2 x 40 ml 0.2 N unbuffered $BaCl_2$ are percolated through it. The percolate is used for the determination of exchangeable Ca, Mg, K and Na. After removal of surplus $BaCl_2$, adsorbed Ba is replaced by 0.2 N $MgCl_2$ solution. Ba in the second percolate is assessed by means of an AAS.

Results of both methods correlate as follows:
- the 33 samples from Zambia (Fig. 2)

$$Y = 0.7634 + 0.9409 \cdot x$$
$$r = 0.9944 \quad t = 492 \quad \text{and}$$

- the 34 samples from Argentine (Fig. 3)

$$Y = 1.7305 + 0.8329 \cdot x$$
$$r = 0.9920 \quad t = 358$$

whereby Y represents the results ofthe $BaCl_2$-TEA method and x the results of the acetate method.

Somewhat higher values of CEC were obtained using the acetate method than by $BaCl_2$-TEA. The average difference between both methods was 1.74 meq/100 g soil for the non-calcareous samples, and 1.02 meq/100 g for the calcareous and saline samples.
For the non-calcareous soils best agreement between the results of both methods was achieved when CEC was less than 4 meq/100 g soil. When CEC exceeded 10 meq/100 g the acetate method yielded higher values. The highest deviation from the mean was ± 15.2 %, smallest ± 0.7 %.

With the calcareous and saline samples the difference between the results of the two methods was less than 1.0 meq/100 g in 22 out of 34 samples. At high CEC values differences up to 7.6 meq/100 g were found but this difference was just ± 8.3 %, when related to the mean of both results.

From these investigations it may be concluded, that results of CEC determination by $BaCl_2$-TEA and by acetate solution adjusted to pH 8.2 are comparable. The small differences between the results of the two methods may be neglected, provided the CEC of the soil does not exceed 25 meq/100 g soil and no soluble sulphates are present.

In case of saline soils containing soluble sulphates, CEC determination by the $BaCl_2$-TEA solution will produce erroneous results.

Our investigations with 34 saline soils samples from Argentine indicated, that there is significant correlation (r = 0.7106, n = 34, t = 8.2) between soluble SO_4^{--} and the difference between the CEC results. (Fig. 4).

However, soluble SO_4^{--} at concentration less than 2 meq/100 g soil does not substantially effect the results of CEC assessment. These findings were confirmed by the result of Labex rounds 85-1/2 and 86-1 (see § 3.4)

3.3 Determination of exchangeable Cations

3.3.1 Assessment of exchangeable Calcium

3.3.1.1 Noncalcareous soils

The assessment of exchangeable Calcium by $BaCl_2$-TEA and NH_4-acetate for the 33 non-calcareous soil samples from Zambia showed the following correlation

$$Y = 0.8788 + 0.7283 \cdot x$$
$$r = 0.9190$$

The regression line (Fig. 5) shows disagreement with the ideal fit when all 33 pairs of data are considered. However, for 25 of the samples the deviation between results of the two methods tested is less than 1 meq/100 g soil. The results of these 25 samples correlate according to

$$Y = -0.0553 + 0.9761 \cdot x$$
$$r = 0.9982$$

The agreement of results obtained by the two methods is excellent.

Deviations of more than 1 meq/100 g soil occur with the two samples containing 0.2 % $CaCO_3$ and with 6 samples originating from horizons affected by groundwater. These samples yielded higher values of exchangeable Ca when treated with NH_4-acetate adjusted to pH 7.0 than with $BaCl_2$-TEA buffered at pH 8.2.

3.3.1.2 Calcareous soils

Substantial amounts of Ca were extracted using the NH_4-acetate solution from calcareous and saline soils, represented by the 34 samples from Argentine. In saline soils these amounts surpass the Ca^{++} detected in the saturation extract. The sum of metallic cations (SMC) exceeds the CEC determined.

In soils containing more than 2.5 % $CaCO_3$ an additional 30 to 35 meq Ca^{++} are dissolved by ammonium acetate adjusted to pH 7.0, when compared to $BaCl_2$-TEA buffered at pH 8.2. The difference between the results for exchangeable Ca obtained by the two methods is independent of the $CaCO_3$ content of the soil.

Nevertheless, when $BaCl_2$-TEA buffered at pH 8.2 is used for the exchange reaction, the amount of Ca^{++} replaced also exceeds the true exchangeable Ca. This follows from the difference between SMC found in the

$BaCl_2$-percolate and the CEC determined. This difference (SMC-CEC) is a function of the $CaCO_3$ content of the soil. If the $CaCO_3$ content is less than 6 %, the difference increases almost linearly with the $CaCO_3$ content. Above 6% $CaCO_3$ the dependence of (SMC-CEC) on the $CaCO_3$ content follows a saturation curve, indicating that the Ca saturation of the $BaCl_2$ solution reaches a maximum (Fig. 6).

For samples containing less then 6 % $CaCO_3$, there is a linear regression between SMC - CEC (Y) and % $CaCO_3$ (x). It follows the equation

$$Y = 1.5823 + 1.1253 \cdot x$$
$$r = 0.7596$$

For samples containing more than 6 % $CaCO_3$ the relation between SMC - CEC and % $CaCO_3$ may be expressed by the function

$$Y = 1.5054 \sqrt{\frac{x}{0.4103}}$$

$$r = 0.8201$$

From the above discussion it may be concluded, that neither NH_4-acetate nor $BaCl_2$-TEA are suitable for exact determination of exchangeable Ca in calcareous soils. Both exchange solutions dissolve Ca from $CaCO_3$ and other calciumsalts contained in the soil. The error is higher with NH_4-acetate than with $BaCl_2$.

The amount of exchangeable Ca in calcareous soils may be calculated from

$$CEC - (Mg^{++} + K^{+} + Na^{+}) = Ca^{++}$$

since in calcareous soils an equilibrium exists between $CaCO_3$ and exchangeable Ca^{++}.

Another possible way to determine exchangeable Ca is to extract Ca and Mg using unbuffered N-KCl solution; this proved to be comparable to extraction by $BaCl_2$-TEA solution when tested with 40 samples from Piaui, Brazil (Fig. 7).

The results of both methods correlated according to

$$Y = 0.33025 + 1.0079 \cdot x$$
$$r = 0.9936$$

Eight of the samples tested contained 0.2 - 2.1 % $CaCO_3$. They yielded higher values for exchangeable Ca when extracted by BaCl - TEA.

A regression curve for (SMC-CEC) vs. % $CaCO_3$ was also drawn for these samples, but correlation was not significant.

Nevertheless, extraction of calcareous soils with unbuffered N KCl seems to provide Ca values, which are more realistic than those obtained using the other extraction methods tested.

3.3.2 Determination of Exchangeable Mg

3.3.2.1 Non-calcareous soils

Comparison of the two methods of determining exchangeable Mg by extraction with $BaCl_2$-TEA and NH_4-acetate yields the following correlation (Fig. 8)

$$Y = - 0.1331 + 0.89133 \cdot x$$
$$r = 0.9885 \quad n = 33$$

Exchangeable Mg determined by the NH_4-acetate method tended to be higher than Mg exchanged by $BaCl_2$-TEA. In 28 out of 33 samples the difference was less than 1 meq/100 g. The five samples, showing a difference above 1 meq were Dambo soils, i.e. vertisols affected by groundwater. Subsoil samples from these profiles also showed deviations in exchangeable Ca, as was mentioned above.

3.3.2.2 Calcareous and saline soils

In general exchangeable Mg determined by NH_4-acetate tends to be somewhat higher than Mg assessed by $BaCl_2$-TEA. The average difference between the results obtained from the two methods for the 35 samples is 0.54 meq. The maximum difference is 1.2 meq/100 g (Fig. 9).

The linear regression follows

$$Y = 0.1217 + 0.7661 \cdot x$$
$$r = 0.9622$$

The coefficient of correlation shows a fairly high degree of significance.

For Mg-determination comparison of the two methods using N-KCl and $BaCl_2$-TEA yielded the following correlation (Fig. 10):

$$Y = 0.1786 + 0.968 \cdot x$$
$$r = 0.9949$$

3.3.3 Determination of exchangeable K

The amount of exchangeable K in the 33 noncalcareous samples from Zambia was too low; therefore only the calcareous and saline soils were used for the comparison of exchangeable K determinations. It turned out, that there is a close correlation between the results of NH_4-acetate and $BaCl_2$-TEA extraction methods. The NH_4-acetate method yielded slightly higher results. The average difference for 35 samples was 0.29. The maximum difference was 0.9 meq/100 g soil (Fig. 11).
The regression line is

$$Y = 0.0302 + 0.7842 \cdot x$$
$$r = 0.9895$$

The results may be regarded as closely comparable.

Determination of exchangeable K using 0.05 N HCl/0.025 N H_2SO_4 as an extractant, resulted in K values of only half those obtaines using $BaCl_2$-TEA extraction. There is of course a clear regression line, but pairs of points are scattered along it (Fig. 12).

The cause of the scatter may be related to the difference in diameter of the hydrated cations involved. There are indications that Ba replaces K more easily from expandable clay minerals than H_3O-ions. This assumption is supported by the fact that the difference between exchangeable K determined by the two methods is greater, the higher the amount of illite and smectite.

3.3.4 Assessment of exchangeable Na

Despite the high and fairly variable amounts of soluble Na salt in the saline soil from Conlara Valley, there were only small deviations between the analyses of exchangeable Na determined by NH_4 acetate and $BaCl_2$-TEA (Fig. 13). The results obtained by both methods correlate according to

$$Y = 0.2056 + 1.064 \cdot x$$
$$r = 0.9961 \quad n = 35$$

There is also a good correlation when exchangeable Na is determined by 0.05 N HCl + 0.025 N H_2SO_4 and $BaCl_2$-TEA (Fig. 14). The results obtained correlate according to

$$Y = 0.00103 + 1.0551 \cdot x$$
$$r = 0.9906 \quad n = 82$$

3.4 Comparison of results of $BaCl_2$-TEA and Acetate-treatment with samples of Labex round 85-1/2 and 86-1

The investigation of 15 samples in Labex round 85/1 and 85/2 as well as the examination of the 10 soil samples in Labex round 86/1 generally confirm the above mentioned findings. The 25 samples represent different soil taxa. When samples 11 and 34, which contain 32.1 and 43.1 meq soluble sulphate respectively were excluded the correlation between the results of the $BaCl_2$ TEA treatment and the Na- acetate treatment were

$$Y = 1.9183 + 0.8514 \cdot x$$
$$r = 0.9788 \quad n = 23$$

and for the round 86-1

$$Y = 1.9308 + 0.8422 \cdot x$$
$$r = 0.9961 \quad n = 2 \times 9$$

The results for exchangeable Ca follow the regression equation

$$Y = 0.4201 + 0.9210 \cdot x$$
$$r = 0.9996 \quad n= 11$$

where only the non-calcareous samples of round 85-1/2 are considered and samples 11, 15, 16 and 23, containing 21.3 %, 27.1 %. 26.3 % and 8.7 % $CaCO_3$ respectively, were omitted from the calculation.

When samples 34 and 36 containing 3.17 and 11.3 % $CaCO_3$ respectively were omitted from correlation of results for round 86-1, the regression line for the 8 remaining samples follows

$$Y = 0.0483 + 1.0403 \cdot x$$
$$r = 0.9984 \quad n = 2 \times 8$$

Regression lines and coefficients of correlation confirm the previous findings that both methods for the determination of exchangeable Ca result in comparable data only, when soils containing less than 2 % $CaCO_3$ are considered.

Coefficients of correlation for exchangeable Mg assessed by $BaCl_2$ or ammonium acetate were 0.9913 and 0.9997 for the 85 and the 86 rounds respectively.

For exchangeable Na r was calculated to be 0.9815 and 0.9604 respectively.

We think both cations can be determined with sufficient acuracy by either method.

The coefficient of correlation found for exchangeable K is r = 0.9179 for the 1985 rounds and 0.9504 for the 1986-1 round. These coefficients are somewhat unsatisfactory and may be due to very low exchangeable K in most of the samples analysed. Determination of exchangeable K is thus not sufficiently accurate.

IV Conclusions

From the results of our investigations it may be concluded that determination of CEC and exchangeable cations by treatment with $BaCl_2$-TEA (pH 8.2) as suggested by Mehlich (1942) or sodium acetate (pH 8.2) and subsequently by ammonium acetate (pH 7.0) as suggested by Bouwer et al. (1952) will yield comparable results provided the following conditions are met:

- The different kinds of cation used for replacement of adsorbed cations and for saturation of the soil have little effect on the resulting CEC and amount of exchangeable cations, thus the differences in absorption capacity due to differences in affinity may be neglected.

- Many soils have variable charge meaning that the adsorption capacity varies with pH. It is therefore of great importance to adjust the pH of the exchanging solution correctly in order to reach potential CEC as a comparable soil parameter.

- The CEC of saline soils that contain above 1.0 meq soluble sulphate should not been determined by using any salts containing Ba as an extractant. Precipitation of $BaSO_4$ will prevent correct determination of the adsorbed Ba. Determination of CEC in these soils should be carried out using sodium-acetate.

- For calcareous soils containing more than 2% $CaCO_3$ neither ammonium acetate nor $BaCl_2$-TEA yield accurate figures for exchangeable Ca due to the fact that both extractants dissolve greater or lesser amounts of Ca from the $CaCO_3$. If calculation of exchangeable Ca from CEC minus (Mg + K + Na) does not meet the requirements, exchangeable Ca in calcareous soils should be extracted using a solution of N KCl or other neutral reacting salt.

- Patience and great care should be taken when preparing the standard solutions and calibraton curves required for the different tests. Due to the fact that a surplus of the extracting salts is present in the percolate or filtrate, which may interfere with measurement of the required ion; it is also important that the standard solutions be adjusted to have an equivalent composition to the exchanger solution used for testing the soil.

The wide variation in the results reported for round 85-2 indicates that even when the methods are standardized, no absolute agreement between the results from different laboratories is achieved.
The skill and experience of the laboratory assistants, as well as the conditions in the laboratory, i.g. the climatic conditions, the type and state of the laboratory equipment, the quality of the water amongst other factors may be of greater importance than standardization of methods used.

However, if soil classification is to be based on analytical data, the methods used to obtain the data have to be quoted in order to help the soil scientist assess the results critically.

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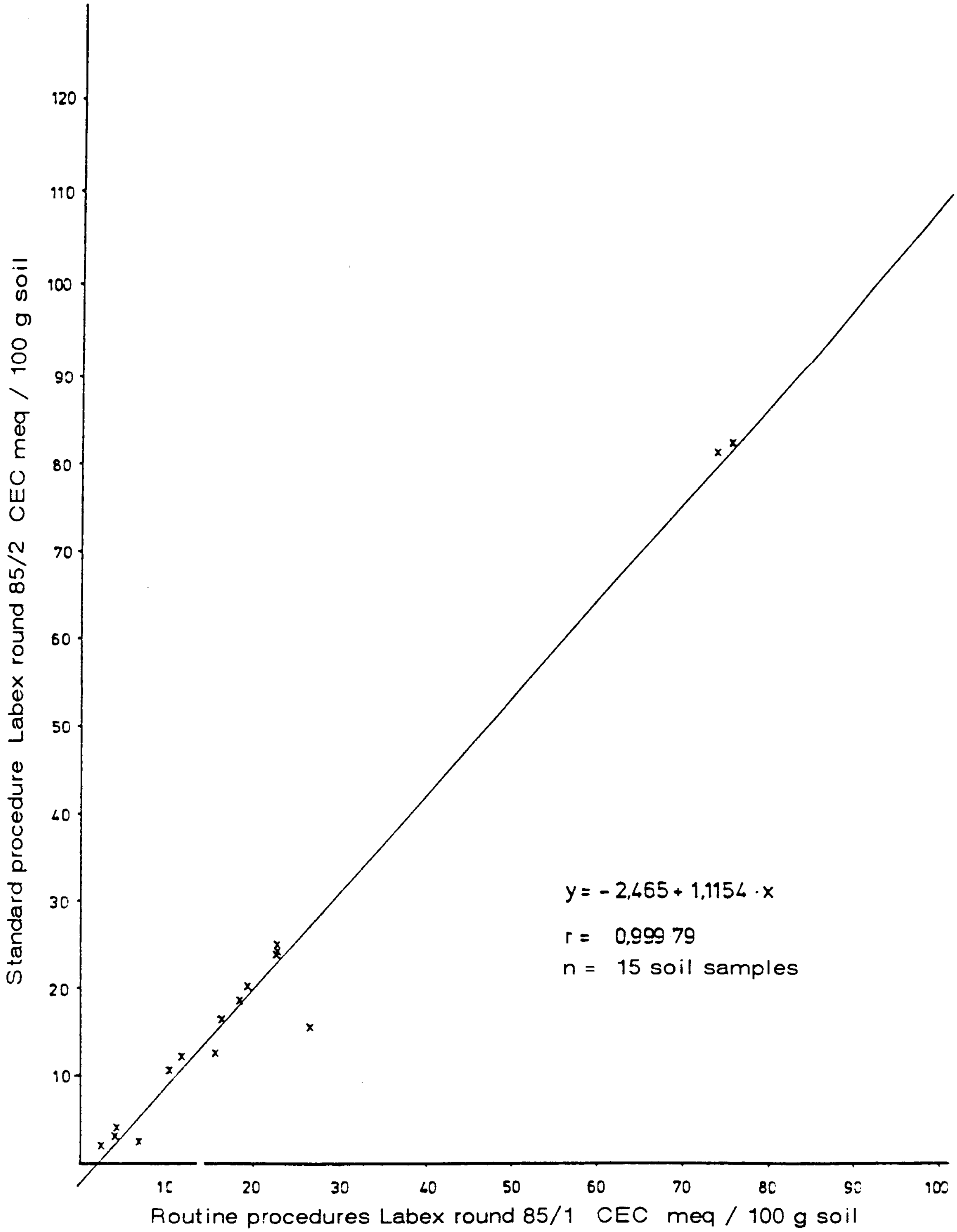

Fig. 1: CEC assessment Routine procedures (Labex round 85/1) vs. Standard procedures (Labex round 85/2)
Mean of 30 participating laboratories

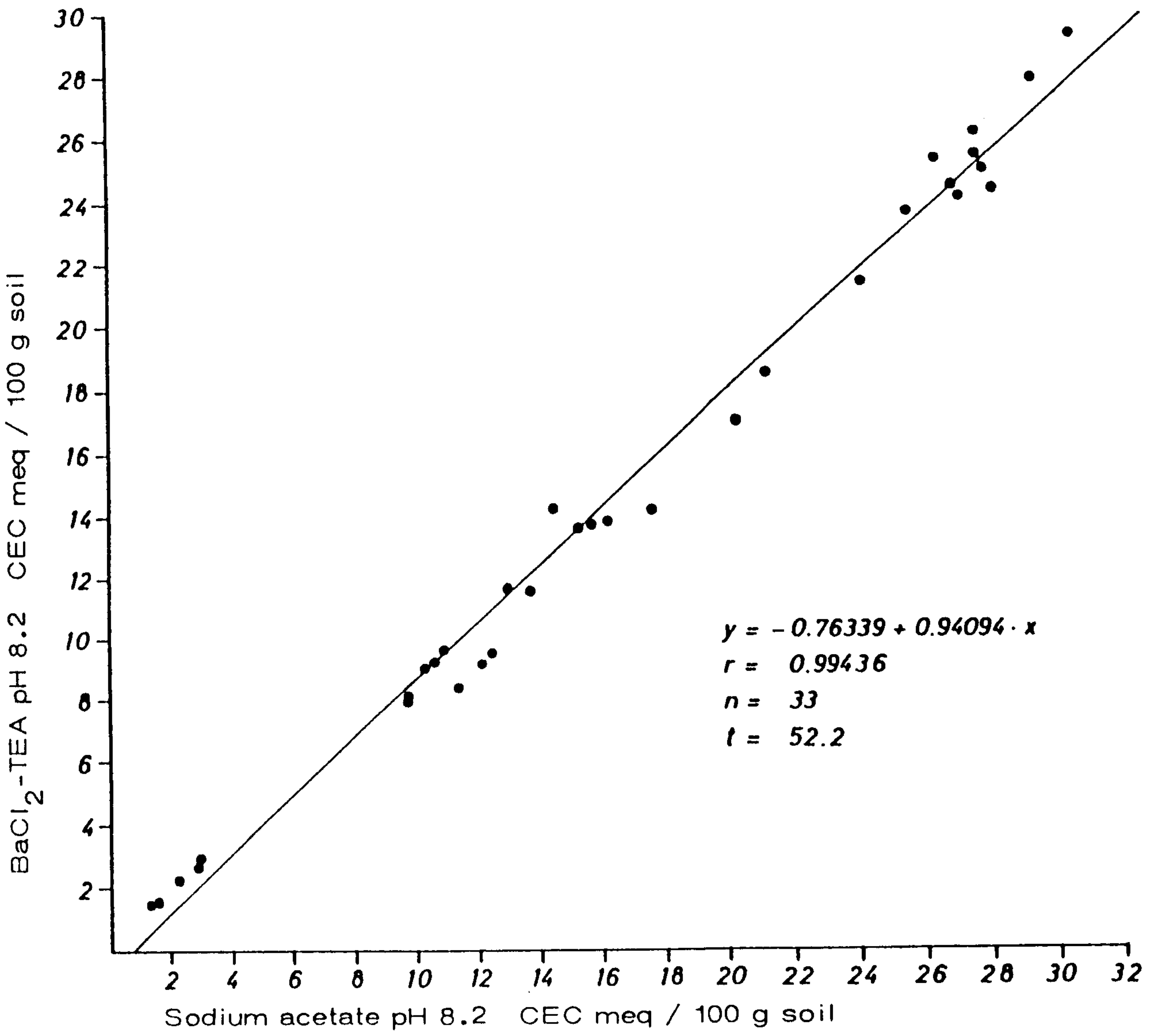

Fig. 2: CEC assessment. Noncareous soils $BaCl_2$ - TEA pH 8.2 (Mehlich 1942)
vs. Na - Acetate (Brouwer et al., 1953)
Soils: Munkumpu, Zambia. 33 samples

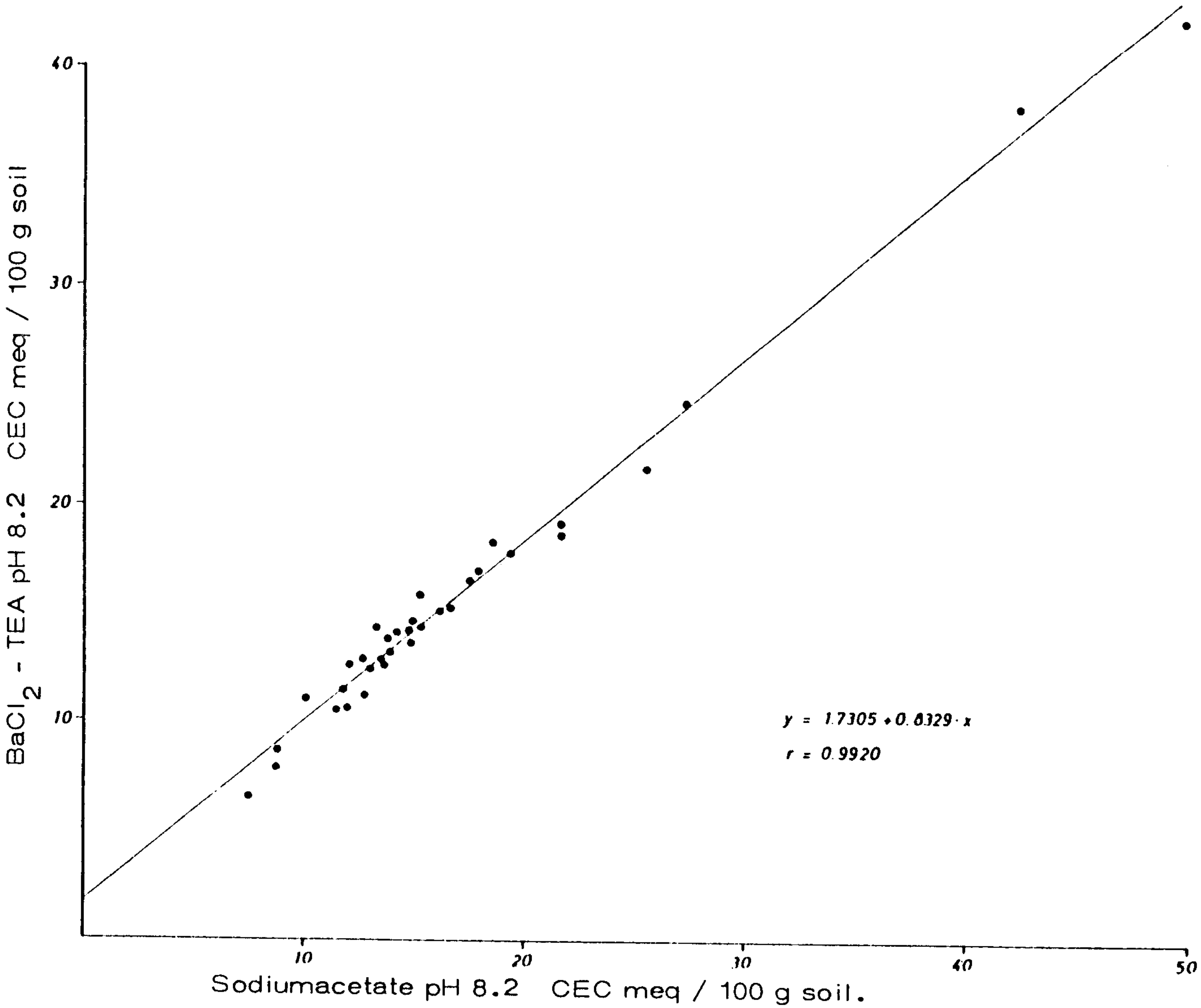

Fig. 3: CEC assessment. Calcareous & saline soils.
BaCl$_2$- TEA (Mehlich, 1942) vs. Na - Acetate (Brouwer et al., 1953)
Soils: Conlara Valley, Argentine. 34 samples

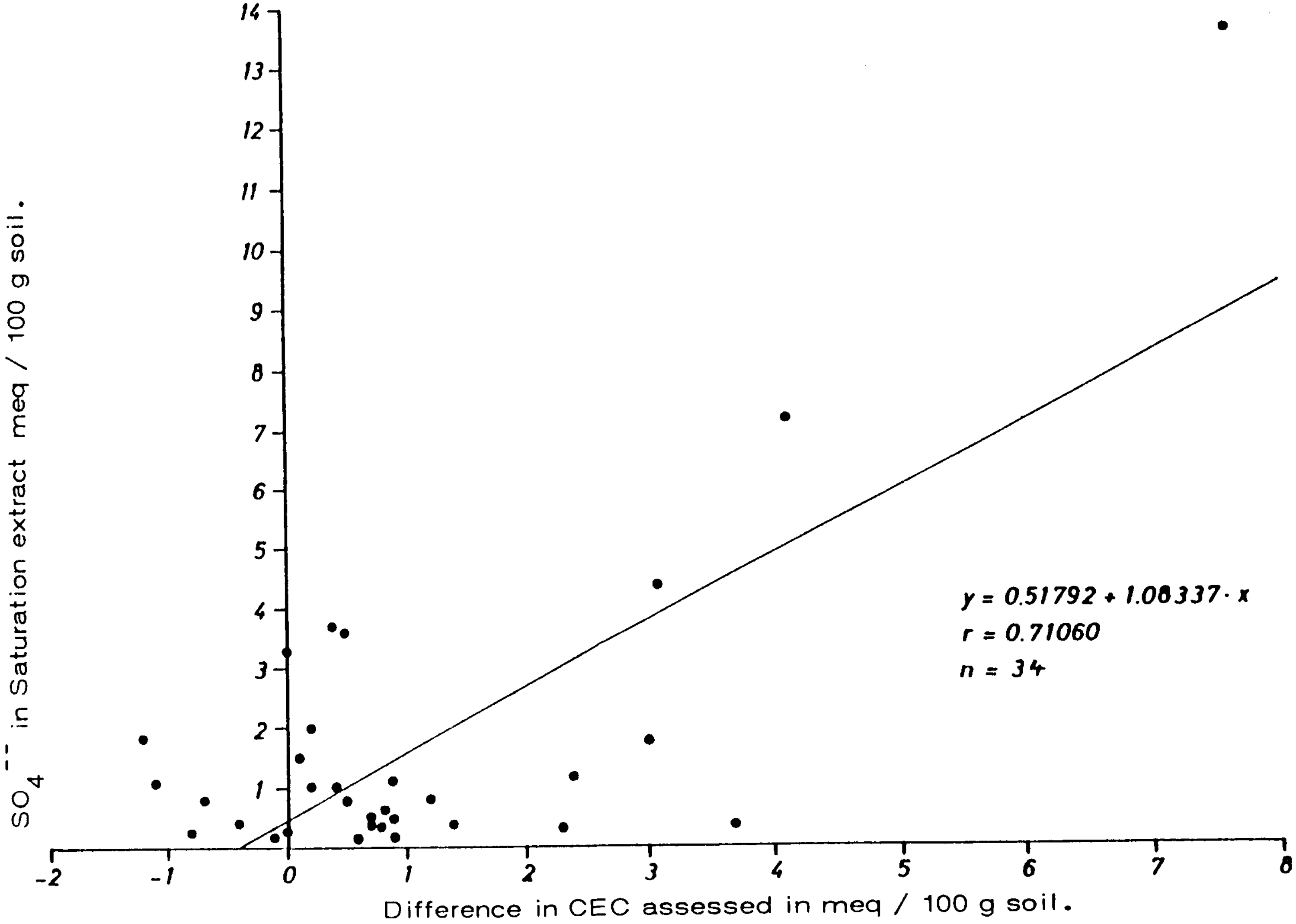

Fig. 4: CEC assessment. Calcareous & saline soils. SO_4^{--} in Saturation extract vs. Difference of CEC assessed by $BaCl_2$ - TEA and Sodiumacetate.
Soils: Conlara Valley, Argentine. 34 samples

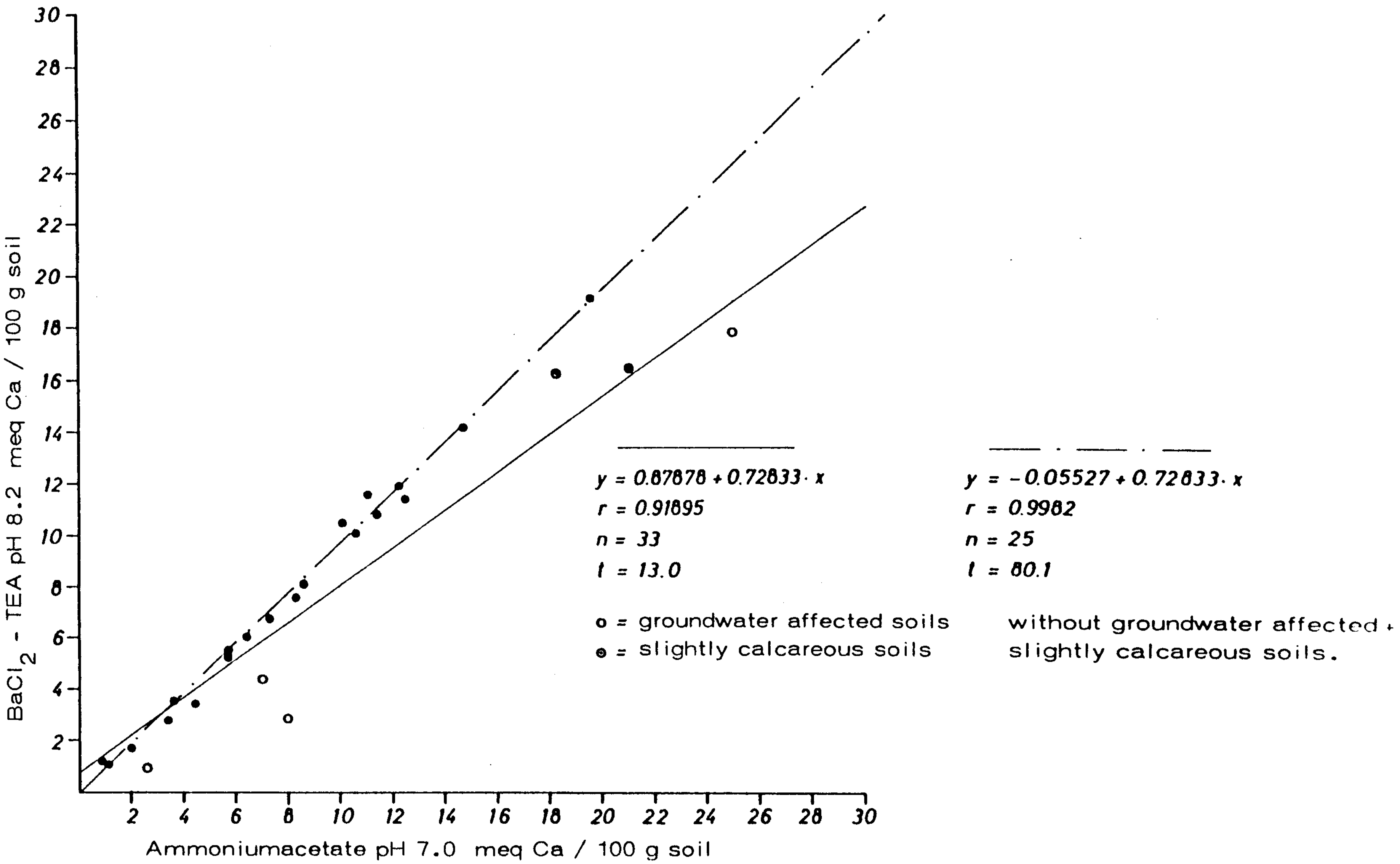

Fig. 5: Assessment of exchangeable Calcium. Noncalcareous soils
$BaCl_2$ - TEA pH 8.2 (Mehlich, 1942) vs. NH_4 - Acetate pH 7.0 (Brouwer et al., 1953)
Soils: Munkumpu, Zambia. 33 samples.

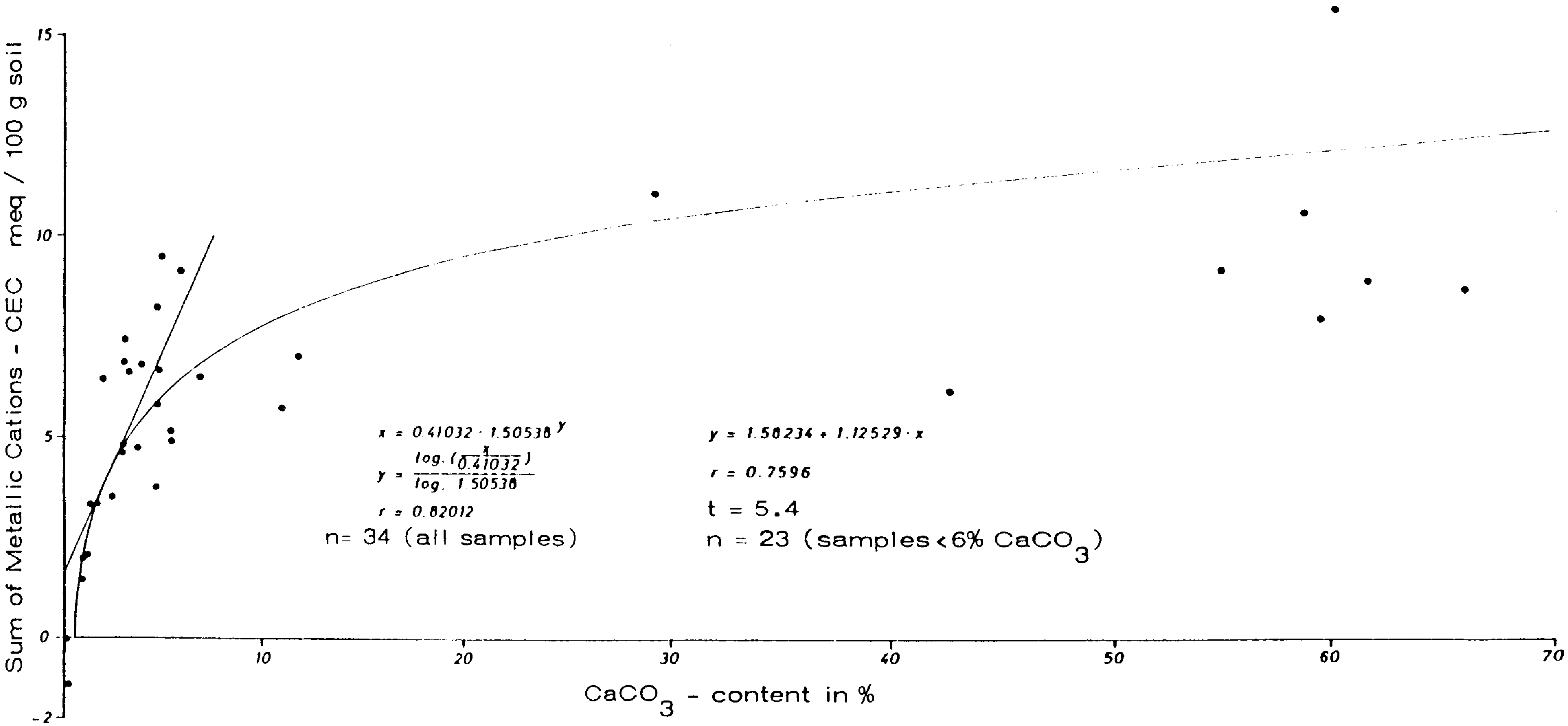

Fig. 6: Assessment of exchancheable Ca. Calcareous & saline soils. Sum of Metallic Cations - CEC, determined by $BaCl_2$ - TEA pH 8.2 (Mehlich, 1942) vs. $CaCO_3$ - content of soil.
Soils: Conlara Valley, Argentine

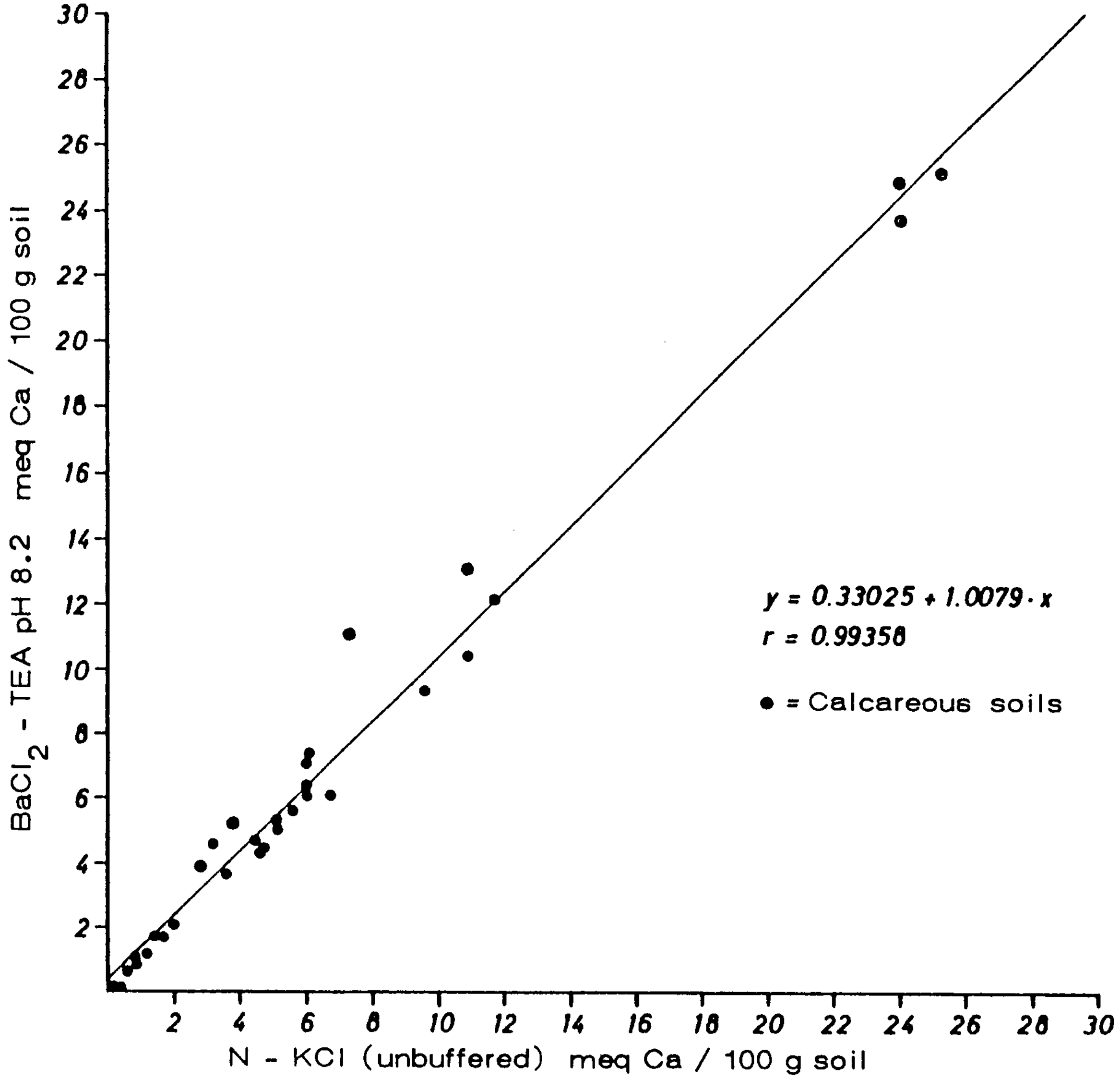

Fig. 7: Assessment of exchangeable Ca. $BaCl_2$ - TEA pH 8.2 vs. N - KCl solution. Soils: Piaui, Brazil. 40 samples

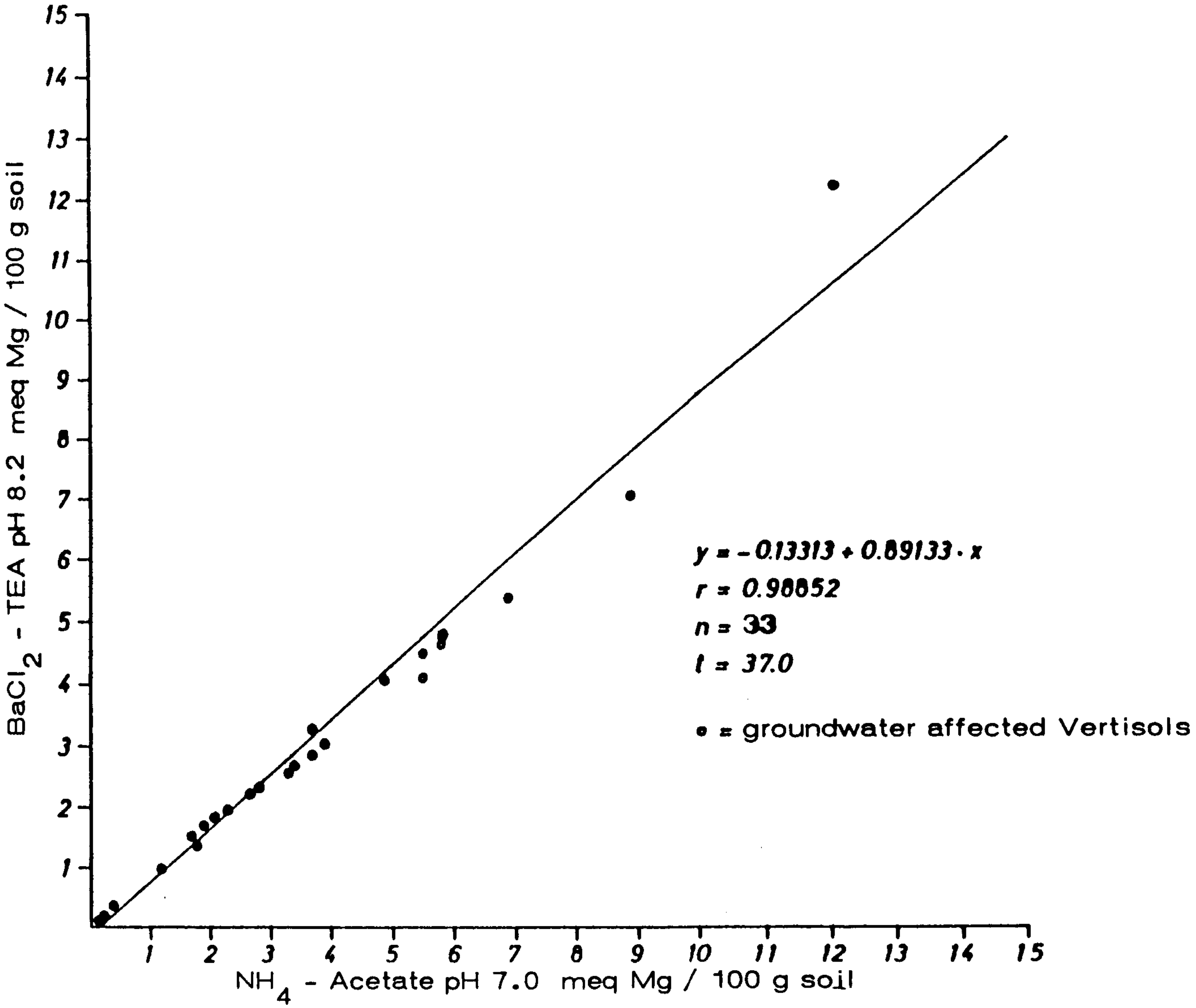

Fig. 8: Assessment of exchangeable Mg. Noncalcareous soils.
BaCl$_2$ - TEA pH 8.2 (Mehlich, 1942) vs. NH$_4$ - Acetate (Brouwer et al., 1953).
Soils: Munkumpu, Zambia. 33 samples.

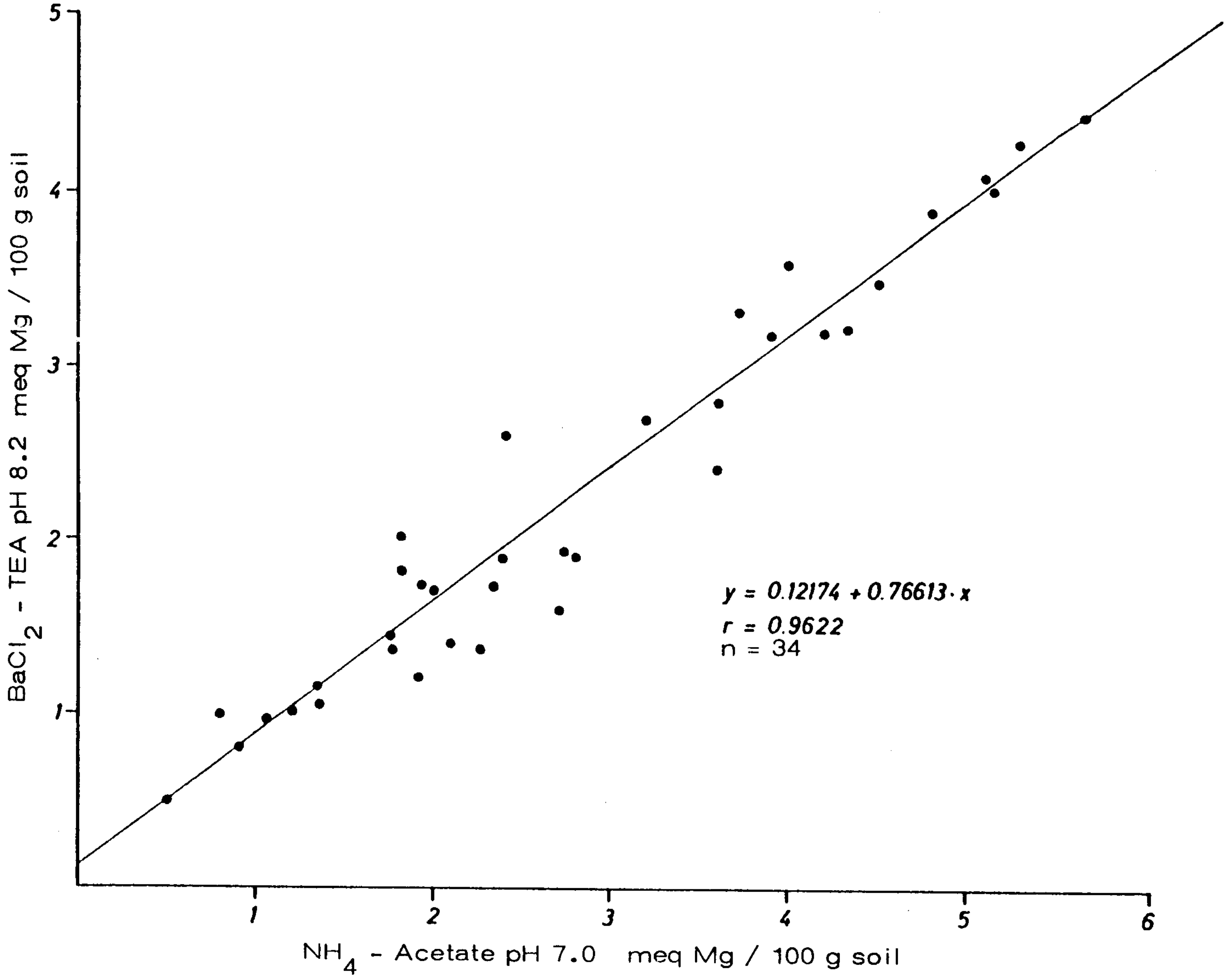

Fig. 9: Assessment of exchangeable Mg. Calcareous & saline soils.
$BaCl_2$ - TEA pH 8.2 (Mehlich, 1942) vs. NH_4 - Acetate pH 7.0 (Brouwer et al.,1953)
Soils: Conlara Valley, Argentine. 34 samples.

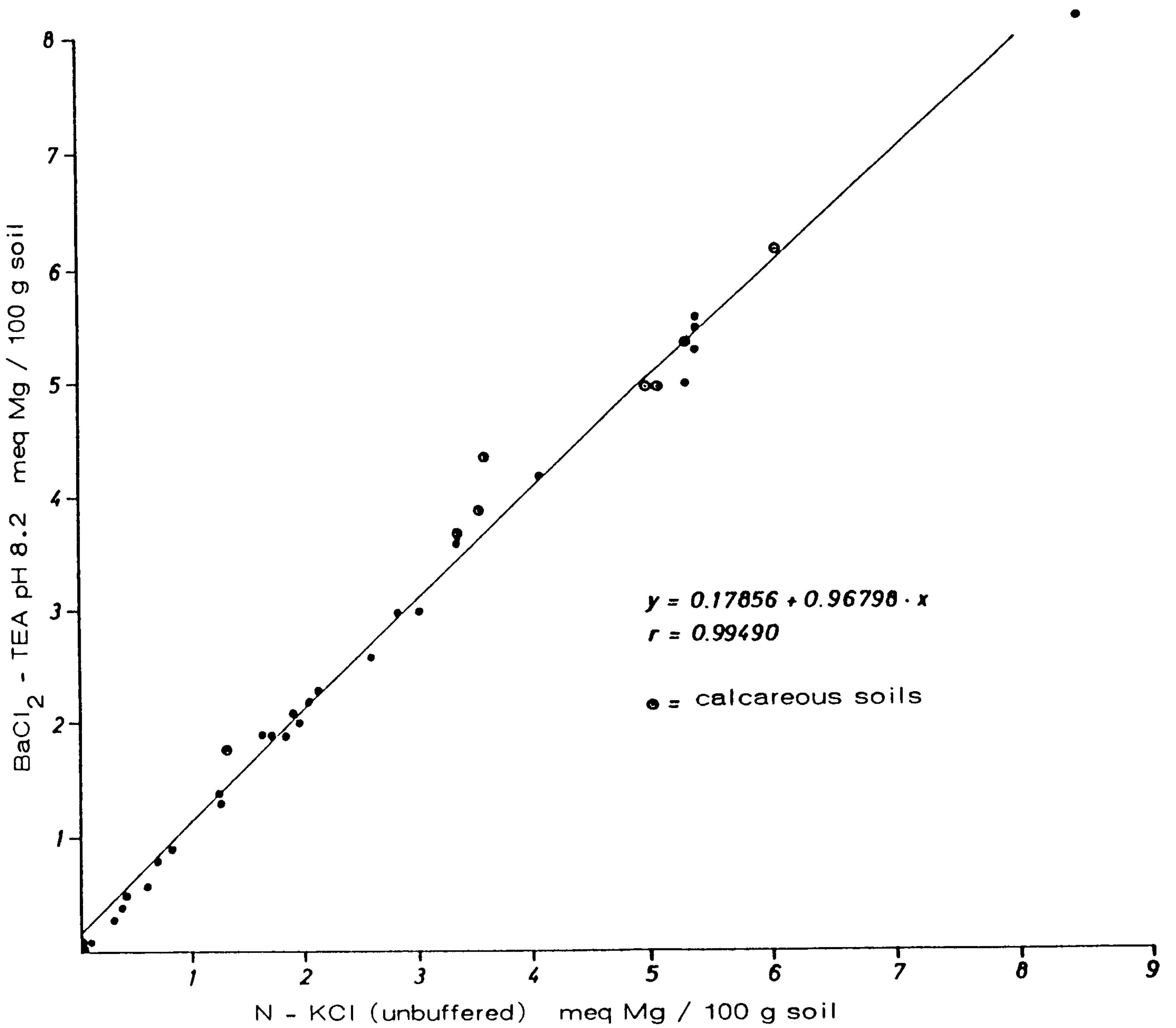

Fig. 10: Assessment of exchangeable Mg. $BaCl_2$ - TEA pH 8.2 vs. N - KCl - solution
Soils: Piaui, Brazil. 40 samples.

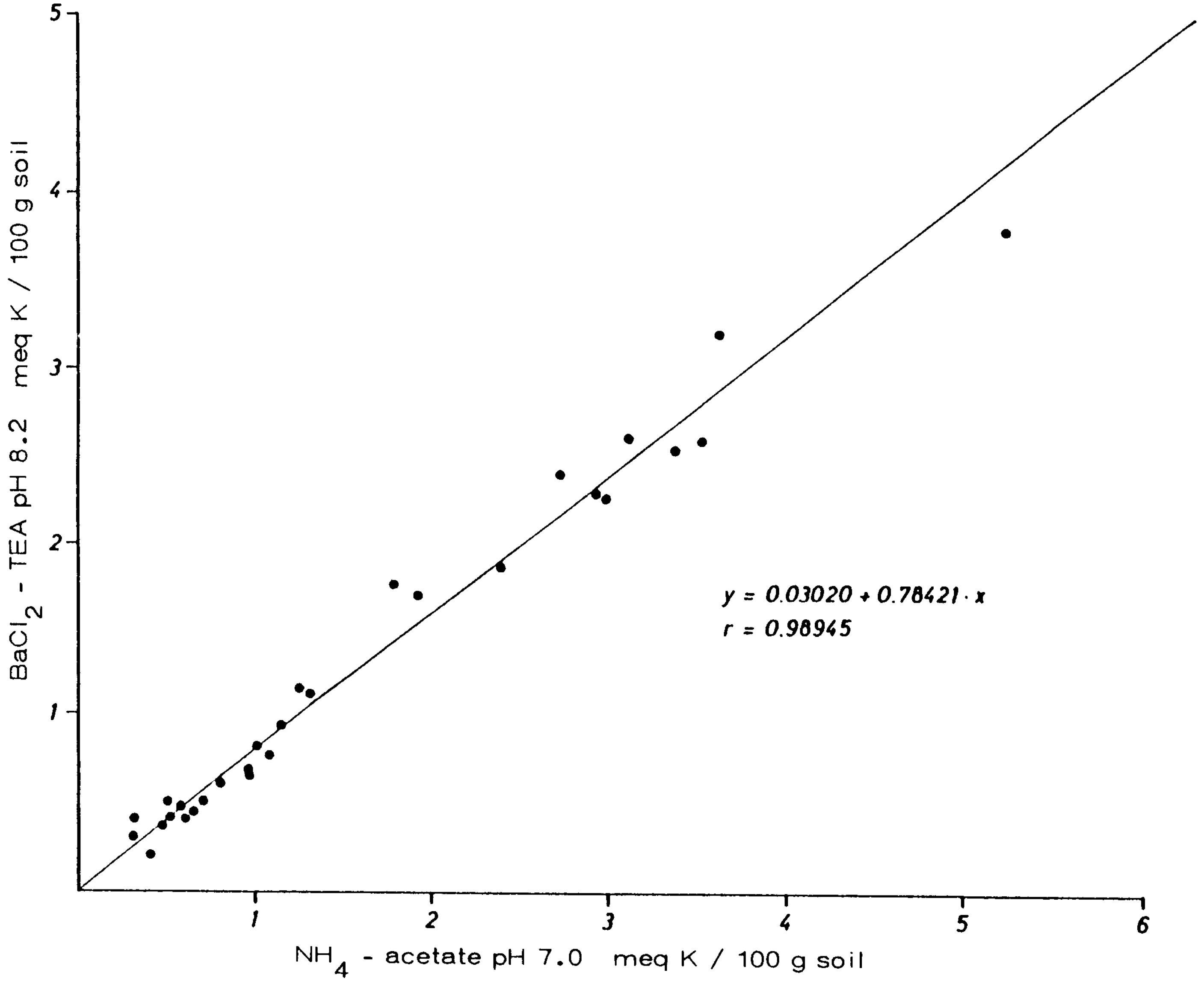

Fig. 11: Assessment of exchangeable K. Calcareous & saline soils.
BaCl$_2$ - TEA pH 8.2 (Mehlich, 1942) vs. NH$_4$ - Acetate (Brouwer et al., 1953)
Soils: Conlara Valley, Argentine. 34 samples.

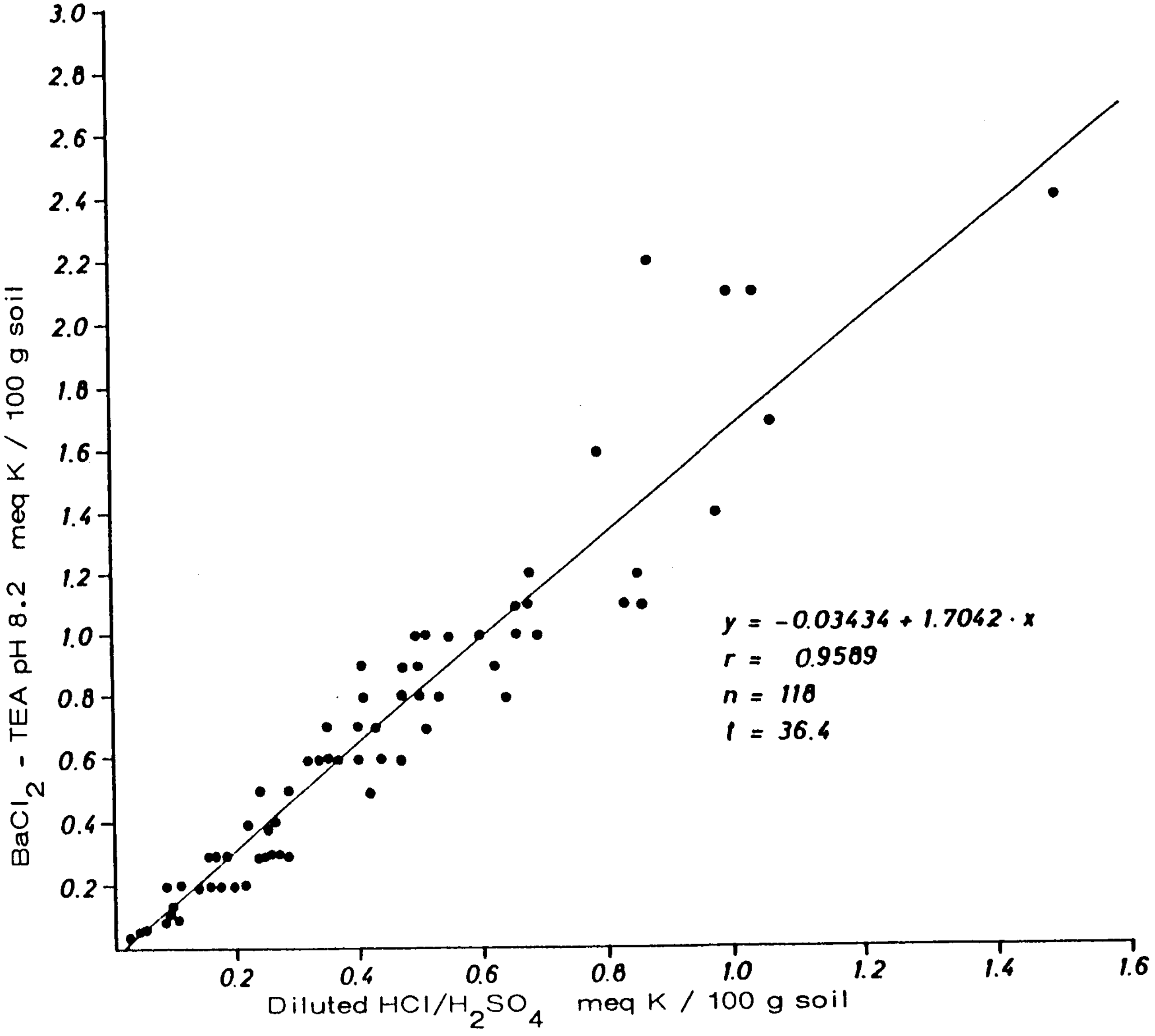

Fig. 12: Assessment of exchangeable K.
$BaCl_2$ - TEA pH 8.2 (Mehlich, 1942) vs. HCl/H_2SO_4 (diluted)(Mehlich No 1)
Soils: Piaui, Brazil. 118 samples

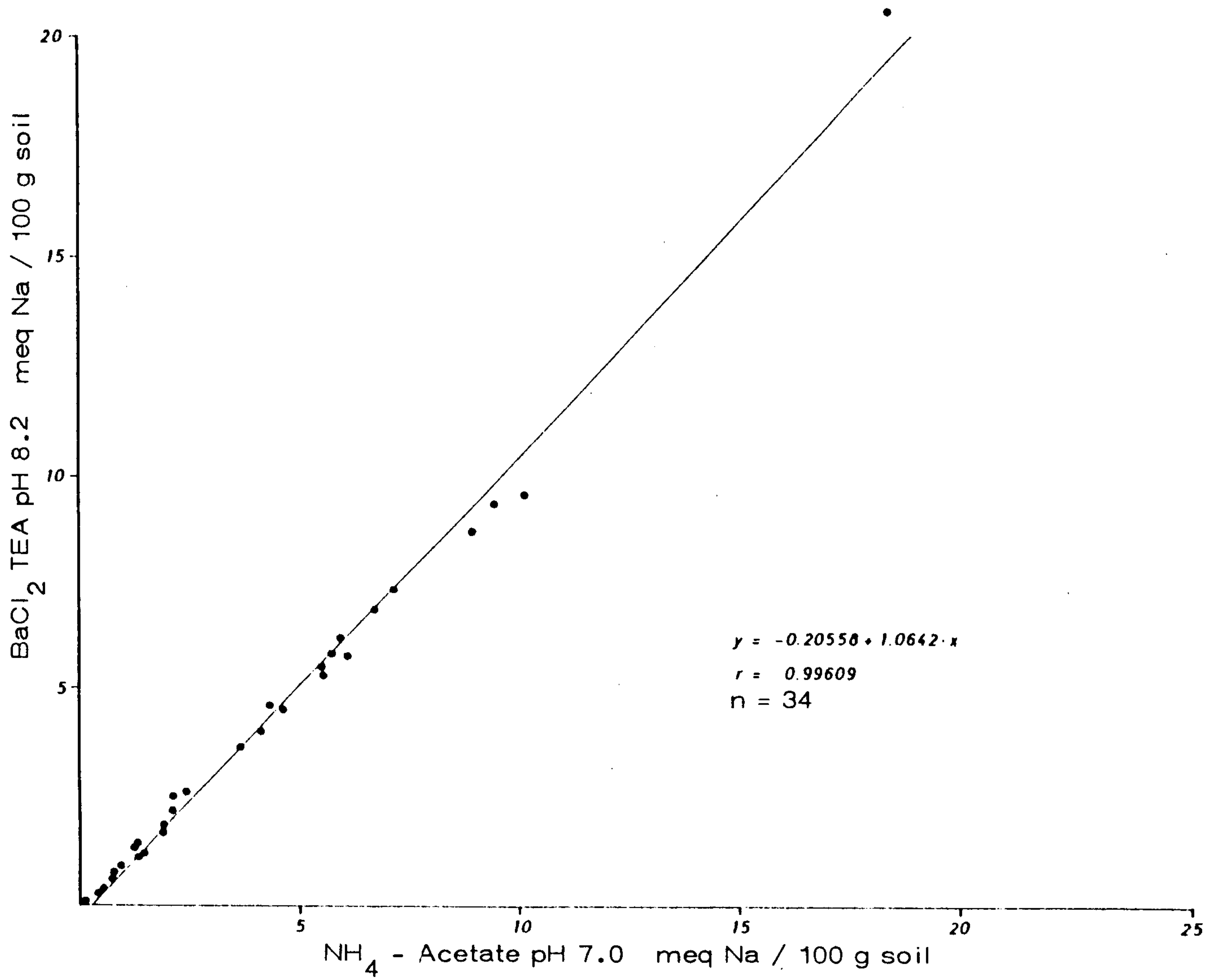

Fig. 13: Assessment of exchangeable Na. Calcareous & saline soils
$BaCl_2$ - TEA pH 8.2 (Mehlich, 1942) vs. NH_4 - acetate (Brouwer et al., 1953)
Soils: Conlara Valley, Argentine. 34 samples

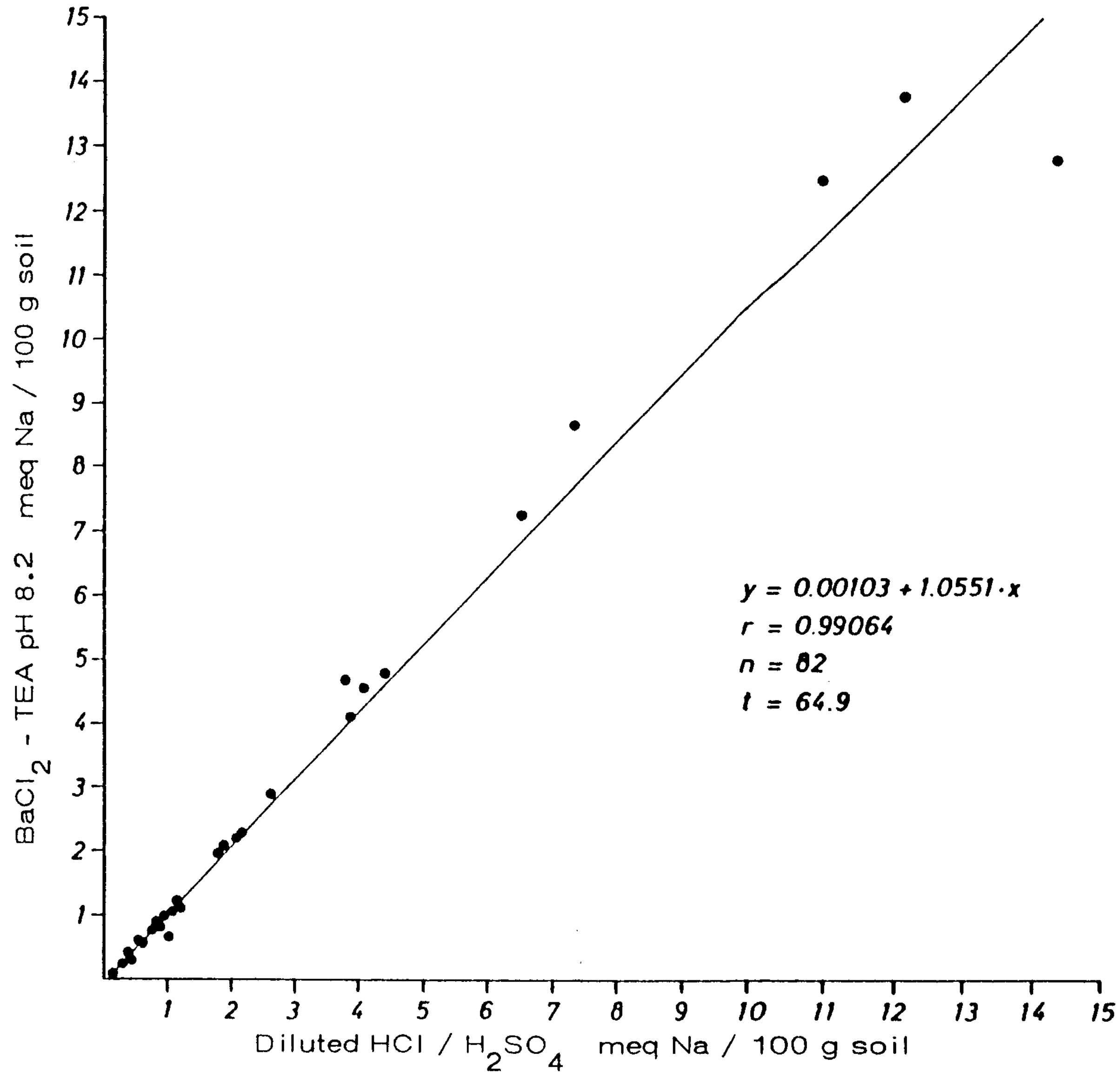

Fig. 14: Assessment of exchangeable Na
BaCl$_2$ - TEA pH 8.2 (Mehlich, 1942) vs. diluted HCl / H$_2$SO$_4$ (Mehlich No 1)
Soils: Piaui, Brazil. 82 samples.

A COMPARISON OF THREE PROCEDURES USED IN PARTICLE-SIZE DISTRIBUTION ANALYSIS OF SOILS

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I Introduction

The solid phase of soil consists of discrete units with varying composition and widely different parameters sometimes called primary particles. For purposes of soil classification primary particles are grouped into specific size ranges on a diameter basis called soil separates.

Two widely used systems for classifying soil separates are:
- the system of the International Society of Soil Science and
- the system of the United States Department of Agriculture.

In this last system 7 categories are distinguished while in the ISSS system only 4 categories are made.

Two principal steps are involved in particle size distribution: dispersion and fractionation. Dispersion is necessary to separate primary particles from each other and it is performed by chemical treatments (H_2O_2 and HCl a.o.) and by mechanical means (stirring). The other important step involved is fractionation where soil particles are sorted into different classes according to size. The most common methods of fractionation are sieving (for particles $> 50 \mu m$) and sedimentation (for particles $< 50 \mu m$). The common methods used in the sedimentation step are the pipette method and the hydrometer method.

II Material and methods

In nine different soils varying in organic matter content (0.1-15.7%C), in pH (2.8-7.8), in carbonate content (0-6%) and in CEC (7-25 $cmol(+)kg^{-1}$) the granular composition was determined according to the pipette method and the hydrometer method. The latter procedure was performed with and without chemical treatment, i.e. digestion of organic matter with 30% H_2O_2 and dissolution of cementing agents with diluted HCl.

III Results

Only in soils high in organic matter the fraction > 50 µm was higher in case no organic matter was oxidized. For comparable data of the fractions < 50 µm it was necessary to sieve off the fraction > 50 µm first.
Generally the hydrometer method gave somewhat higher results for the clay fraction (< 2 µm) and somewhat lower results for the silt fraction (< 20 µm).
Drying of the soils samples up to 100°C of already air-dry soils for a short period of time did not affect the particle size distribution appreciably.

Reference

Mlay, E.D.M., 1985. A comparison of three procedures used in particle-size distribution analysis in soils. Thesis MSc-Course Soil Science and Water Management, Wageningen Agricultural University. 23pp.

A FINAL STEP ALTERNATIVE FOR DIRECT CARBON ANALYSIS IN SOIL

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I Introduction

Just like cation exchange parameters carbon is an important parameter in soil classification and characterization and it has got priority in the LABEX programme as well.

In the beginning of the years 1970 an investigation was started at our Department of Soils and Geology on the genesis and properties of acid sulphate soils. This is an important research topic as these soils are usually in use for rice growth in developing countries in coastal areas with a dense population. Thoughtless management, due to lack of knowledge of the behaviour of these soils, may seriously hamper crop production. Acid sulphate soils are usually strongly reduced, specially in lower parts of the profile where pyrite may occur. The Schollenberger method we commonly used for carbon analysis, could not be used for these soils mainly due to the presence of pyrite (FeS_2), which may react with the oxidator to form sulphate. Therefore we had to shift to an other method.

II Survey of existing methods

Methods for the determination of Organic Carbon all have in common the oxidation of the organic C to CO_2. The oxidation can occur by dry combustion or by wet combustion. The C is determined by a direct measurement of the formed CO_2, or by an indirect measurement, e.g. weight loss of the sample, or excess of the added oxidator.

1. <u>Dry combustion</u>
1.1 Indirect method
    1.1.1 Loss on ignition
        temperature: 850°C
        detection by weight loss
        recovery: 100% (after possible correction)
        recommended for sandy and peat soils only
1.2 Direct methods
    1.2.1 LECO (Tabatabai and Bremner 1970)
        temperature: 1400-1600°C
        detection of CO_2 by thermal conductivity (IR)
    1.2.2 USDA (Soil Investigation Report no 1)
        temperature: 1000°C
        detection of CO_2 by gravimetry (after absorbtion)
        recovery: 100%

2. <u>Wet combustion</u>
2.1 Indirect methods
    2.1.1 Use of $K_2Cr_2O_7$ + H_2SO_4
    2.1.1.1 Walkley Black
        heat source: spontaneous heat of dilution
        detection: titration with Fe^{2+} of excess $K_2Cr_2O_7$
        recovery: factor 1.42 - 1.19 (1.3)

2.1.1.2 Kurmies
heat source: boiling waterbath
detection: titration with $KMnO_4$ of excess Fe^{2+} over $K_2Cr_2O_7$
recovery: 98%

2.1.1.3 Schollenberger
heat source: external, 175°C
detection: Cr^{3+} (colori- or titrimetric)
recovery: 86.9%

2.1.2 Use of $KMnO_4$ + H_2SO_4

2.1.2.1 Ischtscherokow
heat source: boiling waterbath
detection: oxidation of excess $KMnO_4$ with oxalic acid; titration of excess ox.acid with $KMnO_4$
recovery: unknown

2.2 Direct methods

2.2.1 Use of $K_2Cr_2O_7$ + H_2SO_4 + H_3PO_4 (3:2)

2.2.1.1 Allison
heat source: external, 210°C
detection of CO_2 by gravimetry (in absorbent)
recovery: 100%

INTERFERENCES

Loss on ignition:
$CaCO_3$, H_2Oclay, NaCl, S^{2-}, hydr.Fe Al oxides
(44%) (9%) (55%)

Wet combustion (indirect methods):
all oxidizable compounds in the soil: Fe^{2+}, Mn^{2+}, Cl^-, S^{2-} (usually low in concentration)

Allison (direct method):
Cl : KJ 50%
Cl + H_2S : sat. Ag_2SO_4
H_2O : conc. H_2SO_4
$Mg(ClO_4)_2$ or 'anhydrone'
acid fumes : granular zinc

traps in carbon train

REACTIONS

$$\begin{array}{rl} 3\,C \rightarrow 3\,C^{4+} + 12\,e & \\ 4\,Cr^{6+} + 12\,e \rightarrow 4\,Cr^{3+} & \\ \hline 4\,Cr^{6+} + 3\,C \rightarrow 4\,Cr^{3+} + 3\,C^{4+} & + \end{array}$$

interfering reactions

$$\begin{array}{rl} Fe^{2+} & \rightarrow Fe^{3+} + e \\ Mn^{2+} & \rightarrow Mn^{4+}(7+) + 2(5)\,e \\ 2\,Cl^- & \rightarrow Cl_2 + 2\,e \\ S^{2-} & \rightarrow S^{6+} + 8\,e \end{array}$$

oxidation of pyrite (FeS_2)

$$\begin{array}{rl} Fe^{2+} & \rightarrow Fe^{3+} + e \\ S & \rightarrow S^{6+} + 6\,e \\ S^{2-} & \rightarrow S^{6+} + 8\,e \\ \hline FeS_2 & \rightarrow Fe^{3+} + 2\,S^{6+} + 15\,e \quad + \end{array}$$

$$5\,Cr^{6+} + FeS_2 \rightarrow Fe3+ + 2\,S6+ + 5\,Cr3+$$

III The alternative method for soils containing pyrite

As pyrite is also oxidized during the oxidation of the organic carbon, an indirect method is unsuitable for soils containing pyrite.
At our institute we therefore shifted to the direct method of Allison, however we were not familiar with the outfit of the purifying train and absorbent traps needed for this method. We worked out an alternative method which embodies the total wet combustion step of Allison but with a different kind of absorption and detection of the evolved CO_2.

This alternative was published in the Analyst (Begheyn, 1976) and it will be summarized here.
The principle of this detection is to absorb the CO_2 in a solution containing 2.50 mmol NaOH and 0.96 mmol $BaCl_2$. This results in a precipitation of $BaCO_3$. After the sample oxidation is completed 0.99 mmol disodium-EDTA is added to dissolve the $BaCO_3$ and neutralize all OH^-. The pH of the final solution, consisting of BaEDTA and H_2CO_3, is related to the amount of absorbed CO_2 by means of a calibration curve.
The reactions are as follows:

- absorption of CO_2 in NaOH and $BaCl_2$:

$$CO_2 + Ba^{2+} + 2\,OH^- \longrightarrow \underset{\text{(precipitate)}}{BaCO_3} + H_2O$$

- neutralisation and dissolution by EDTA:

$$H_2EDTA^{2-} + Ba^{2+} + 2OH^- \longrightarrow BaEDTA^{2-} + 2H_2O$$
$$H_2EDTA^{2-} + \underset{\text{(precipitate)}}{BaCO_3} + 2OH^- \longrightarrow BaEDTA^{2-} + CO_3^{2-} + 2H_2O$$
$$CO_3^{2-} + H_2O \longleftrightarrow HCO_3^- + OH^-$$

From these reactions can be seen that $BaCl_2$ and EDTA are only intermediates. This method is thus based on the neutralisation of NaOH by the CO_2. The calibration curve can be regarded as a titration graph of NaOH against CO_2.

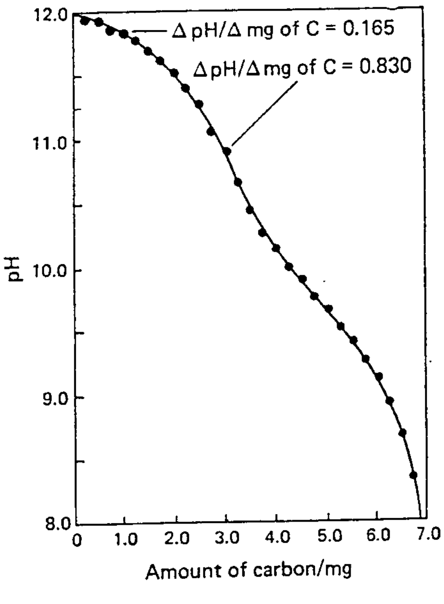

Fig. 1: Relationship between pH and amount of carbon absorbed as carbon dioxide in a solution that is 0.20% m/V in sodium hydroxide, 0.40% m/V in barium chloride and 0.74% in disodium EDTA (pH 12.00 calibrated)
(from Begheyn, 1976)

The absorbtion and detection of CO_2 evolved by the wet combustion procedure of Allison, results in a new method for analyzing carbon in soils in the semi-micro range of 0 - 6 mg C. Interferences are less and thus a troublesome purifying train is not necessary. It proved to be more sensitive and reproducible than the gravimetric step in Allison's procedure. Thus it can be regarded as a final step in the improvement of quantitative organic and inorganic carbon analysis in soils.

Reference

Begheyn, L.Th., 1976. Determination of Organic and Inorganic Carbon in Soils by Potentiometry. Analyst 101: 710-716.

SOIL FERTILITY EVALUATION

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I Introduction

Nutrient availability in soils has been estimated by extracting the soil with various chemical reagents. Extractants are chosen which generally extract a proportionate amount of the total amount available. Interpretation of the available soil nutrient level is based on whether it is adequate or deficient for optimum plant growth. In some instance the soil chemical data obtained for soil characterization can also be used for soil fertility evaluation. This discussion will be divided into three major sections: soil fertility evaluation of base status, anions-phosphate and sulfate, and micronutrient status.

II Soil Base Status

1. Soil Acidity and Lime Requirement

Soils of humid and subhumid regions, in their natural state are generally acid with reaction below pH 5. Crop yields on these soils are low because of the acid soil conditions. In many instances the predominant exchangeable cation in these acid soils is Al which if present in appreciable concentrations in the soil solution is detrimental to plant growth. Exchangeable Al is extracted from soils using a neutral unbuffered salt solution such as KCl. The usual procedure is to extract 10 grams of soil with 50 mls $\underline{M}$ KCl by shaking for 30 minutes, filtering and then washing with another 50 mls of $\underline{M}$ KCl. The filtrate is titrated with 0.1$\underline{M}$ NaOH using phenolphtalein as the indicator. The amount of base used is equivalent to the exchangeable acidity. The proportion of the exchangeable acidity which is Al and H can be determined by the method of Yuan (1959). To the filtrate which has been titrated to the phenolphtalein endpoint add 1 drop of 0.1$\underline{M}$ HCl to make the solution colorless and then add 10 ml of NaF solution (40 g NaF in 1 liter H_2O). Titrate with 0.1$\underline{M}$ HCl until the color just disappears. Add a drop of indicator and if the color returns continue the titration until the color disappears. The titer of 0.1$\underline{M}$ HCl is equal to exchangeable Al. Exchangeable H is equal to exchangeable acidity minus exchangeable Al. In most mineral soils essentially most of the exchangeable acidity is Al.

The interpretation of the exchangeable Al data as to its effect on plant growth is related to the percentage of total exchangeable cations which are Al. The sum of exchangeable Ca, Mg, K, Na, and KCl-replaceable Al+H has been termed the effective cation exchange capacity. When the Al saturation of the effective CEC is greater than 60% there is a relatively high concentration of Al in the soil solution (Table 1). Therefore when the Al saturation is greater than 60% Al toxicity is assumed to be a problem with many crops. A review of liming experiments on Ultisols and Oxisols indicated that when the Al saturation was greater than 60% the growth of corn, wheat, soybean, bean and sweet potato was less than 50% that of the limed treatments (Kamprath, 1984). Optimum growth of most crops is obtained when the Al saturation is less than 10%.

For most crops the approach to liming should be to neutralize the exchangeable Al. For most mineral soils this can be achieved by basing the lime rate on the amount of KCl-extractable acidity. The amount of lime to neutralize a given amount of exchangeable Al is given by the equation: $CaCO_3$ equivalent (T/ha) = Factor x meq acidity/100g. Results of numerous studies has shown that for Ultisols this factor is 2 (Kamprath, 1984). The reason that this factor is greater than 1 is because pH dependent acidity becomes active as the pH increases and reacts with lime (Kamprath, 1970).

2. Calcium Availability

Calcium availability in soil is influenced by the calcium saturation of the cation exchange sites and the presence of toxic amounts of Al, H and/or Mn which inhibit calcium uptake. The amount of exchangeable Ca is generally determined by extraction with NH_4OAc. The availability of exchangeable Ca where soil acidity is not a problem is related to the calcium saturation of the CEC. Maximum root elongation of cotton roots was obtained with 12 percent saturation of the effective CEC and no soil acidity problems (Howard and Adams, 1965). Optimum growth of tropical and temperate legumes was obtained at pH 5.5 with 26 percent Ca saturation of the CEC determined with NH_4OAc (Andrew and Norris, 1961). In most instances liming rates based on neutralization of exchangeable Al will supply adequate amounts of Ca for plant growth.

3. Magnesium availability

Magnesium problems generally occur on low CEC soils with a low reserve of weatherable minerals and pH values of 5 or less. Exchangeable Mg is the major source of plant available magnesium and is extracted with NH_4OAc. The availability of exchangeable Mg is a function of the Mg saturation of the CEC. Soils supplied adequate Mg for plant growth when the Mg saturation of the NH_4OAc determined CEC was 5% (Table 2). This was true over a wide range of CEC.

4. Potassium Availability

The amount of K available for an annual crop is a function of the amount of exchangeable K in the soil. The critical K level for optimum plant growth is in the range of 0.2 to 0.3 meq/100 g soil (Table 3). The higher critical value is generally found with soils having three layer clay minerals which have a stronger affinity for K than 2 layer clay minerals. (Hipp and Thomas, 1967). When the exchangeable K level is less than 0.1 meq/100 g large responses to K fertilization can be expected (Freitas et al., 1966; Boyer, 1972). Soils with micaceous clays have a capacity to supply K for a longer period of time from non-exchangeable forms than soils with primarily kaolinitic clays (Mengel and Kirkby, 1982).

Exchangeable K as determined by extraction with NH_4OAc is a good measure of plant available K (McLean and Watson, 1985). The amount of K extracted with dilute acids, such as 0.1$\underline{M}$ HCl, is correlated with NH_4OAc extractable K and also provides a good estimate of plant available K.

III Phosphate and Sulfate Availability

1. Phosphate availability

Selection of an extractant for estimating available P needs to consider the form of soil P which is the source of plant available P. In acid to neutral soils aluminium phosphates are the primary source of plant P along with any $CaHPO_4$ present (Kamprath and Watson, 1980). The source of P in calcareous soils which is correlated with plant growth is $CaHPO_4$ (Olsen et al., 1954).

The Bray I solution, 0.025M HCl + 0.03M NH_4F, is an excellent extractant of aluminium phosphates because of the strong complexing action of F for Al (Kamprath and Watson, 1980). The Bray 1 solution will also extract $CaHPO_4$. Another extractant for P which is used on Ultisols and Oxisols is the Mehlich 1, 0.05N HCl + 0.025 N H_2SO_4 (Kamprath and Watson, 1980). If calcium phosphates are not present, the Mehlich 1 extracts primarily aluminium phosphates. The Olsen extractant, 0.5M $NaHCO_3$ pH 8.5, was developed for calcareous soils (Olsen et al. 1954). The HCO_3^{-1} replaces HPO_4^{-2} adsorbed on the surfaces of $CaCO_3$. The Olsen method has also been used for weathered soils. The alkaline nature of the $NaHCO_3$ results in hydrolysis of the Al and release of P (Kamprath and Watson, 1980).

Studies with three groups of soils showed that Bray 1 and Olsen extractable P gave the best correlation with labile P of calcareous and slightly weathered soils while Bray 1 and Mehlich 1 gave the best estimates of labile P in highly weathered soils (Sharpley et al., 1984). The highly weathered soils consisted of Oxisols, Ultisols, Ultic subgroups of Alfisols, Quartzipsamments, and acidic Ochrepts.

Critical soil test P levels for the extractants are given in Table 4. The critical level for Bray 1 is in the range of 25 to 36μg g^{-1} for soils which have a low P buffering capacity but for soils with a high P buffering capacity the critical level will be less (Holford, 1980; Novais and Kamprath, 1978).

With the Olsen method the critical P level is approximately 10μg g^{-1}. The critical P level with the Mehlich 1 extractant is dependent upon soil texture which takes into account the P buffering capacity of the soil. For sandy soils the critical P level is in the range of 25 to 30μg g^{-1} while with clayey soils the critical level is 8 to 15μ g^{-1}.

2. Sulfate Availability

Sulfate is the form of sulfur mostly taken up by plants. Sulfate is present in soils as $CaSO_4$ and as sulfate adsorbed by hydrated oxides of Al and Fe. Because sulfate is held in soils by mechanisms similar to that of P, solutions containing phosphate are used to extract sulfate. The common extractant is $Ca(H_2PO_4)_2$ solution containing 500 ppm P and using a soil solution ration of 1:10. Critical levels of phosphate extractable S for plant growth are 8-10 ppm SO_4 -S (Reisenauer, 1975; Blair, 1979).
In assessing the sulfate status of cultivated soils it is necessary to also consider the sulfate level of the subsoil. Sulfates tend to accumulate below the plow layer because phosphates are more strongly adsorbed than sulfates.

IV Micronutrient Status

Soil testing for micronutrients is being more prevalent as crop production becomes more intensified. Micronutrient deficiencies are most apt to occur on the sandy highly leached, acid soils, the highly weathered soils and organic soils. Lindsay and Cox (1985) have made a survey of micronutrient soil testing for the tropics. They have indicated procedures used in various countries and the critical levels used for interpretation of the results. Dilute acids are often used for extracting kaolinitic clays such as Ultisols and Oxisols. However on neutral and calcareous soils, chelating and complexing agents have been used to extract micronutrient cations. Chelating and complexing agents have also been used on acid soils.
Calibration of micronutrient soil tests has been limited. In many instances soil properties need to be considered in the interpretation of the micronutrient soil tests.

1. Micronutrient Cations

Several extractants have been widely used to evaluate the micronutrient cation status of soils, Mehlich 1 and DPTA. The Mehlich 1 solution 0.05 N HCl + 0.025 N H_2SO_4 is used to extract soils as previously described.
The DPTA extractant consists of 0.005M DPTA (diethylene-triaminepentaacetic acid), 0.1M triethanol-amine and 0.01M $CaCl_2$, with a pH of 7.3 (Lindsay and Norvell, 1978). Ten grams of soil are shaken with 20 ml of the DPTA solution for 2 hours and the leachate analyzed for Zn, Fe, Mn and Cu.
The critical soil test levels for Mehlich 1 and the DPTA extractants are given in Table 5. The DPTA was developed for soils that had relatively high pH values (above pH 7.3) but has been used on soils not containing free $CaCO_3$ (Lindsay and Norvell, 1978). The Mehlich 1 has been used primarily with soils having pH values less than 7. The two extractants gave similar critical levels for Zn and Cu. However for Mn the critical values were very different. Mascagni and Cox (1985) found a critical Mn level of 4.7 ppm at pH 6 and 9.7 ppm at pH 7. The DPTA method is not affected as much by pH.

2. Micronutrient Anions

The micronutrient anions, B and Mo, are more difficult to assess by chemical tests as to their plant availability. Boron is generally extracted with hot water. Most critical values for water extractable B are in the range of 0.2 to 1 ppm (Lindsay and Cox, 1985).
The most common extractant for molybdenum is an ammonium oxalate solution (Cox and Kamprath, 1972; Lindsay and Cox, 1985). In most instances, however, there has been a poor correlation between extractable molybdenum and plant growth. Other factors such as soil pH and iron oxide content seem to be more important in determining Mo availability than the oxalate extractable Mo.

V Fertility Capability Classification

A Fertility Capability Classification System (FCC) was developed for "grouping soils according to the kind of problems they present for agronomic management of their chemical and physical properties" (Sanchez et al., 1982). Fertility related constraints considered are CEC, Al saturation, high P fixation, low K reserves, free $CaCO_3$.

The soil fertility modifiers used in the FCC system and their definition are given in Table 6. The e modifier indicates that cations such as K and Mg can be readily leached from these low CEC soils. Soils with an a modifier will have Al toxicity problems and poor availability of phosphorus fertilizers. An h modifier indicates that Al sensitive crops will do poorly.
The b modifier indicates P fixation by $CaCO_3$ and possible Zn and Fe deficiencies. Soils with the k modifier have low K supplying power from nonexchangeable sources. The i modifier indicates a soil with high P fixing capacity.

VI Recommendations for Labex

- The chemical determinations made for soil classification purposes provide a great deal of information which can be rised for soil fertility evaluation. These data are CEC, exchangeable Ca, exchangeable Mg, exchangeable K organic matter, and soil pH.
- Exchangeable acidity (Al + H) should be determined by extracting the soil with $\underline{M}$ KCl and titrating the extract with NaOH to the phenolphtalein endpoint. The exchangeable acidity can be divided into Al and H by appropriate procedures. Effective CEC is the sum of exchangeable bases and exchangeable acidity. The calculation of percent Al saturation should be based on the effective CEC.
- Consideration should be given to determination of available soil phosphorus. Methods which can be used are Bray 1, Mehlich 1 and Olsen. The Bray 1 and Mehlich 1 methods are well suited for non-calcareous soils in which Al-P and Fe-P are the main forms of inorganic P. The Olsen method is adapted for calcareous and is also suited for non-calcareous soils.
- Micronutrient determinations should not be requested at present as part of the Labex programme. Individual laboratories may want to determine micronutrientents.

Table 1 - Exchangeable Al saturation and soil solution Al concentration of acid Ultisols and Oxisols.

Area	Soil	pH	Exch.Al	ECEC	Al.Sat.	Al Soil Solution
			meq/100 g		%	µg/ml
Brazil (1)	Haplustox	4.5	1.15	1.64	70	1.6
Nigeria (2)	Paleudult	4.2	1.83	2.86	64	3.0
N. Carolina (3)	Paleudult	4.6	3.67	4.77	77	5.5
Puerto Rico (4)	Oxisol	4.1	5.35	6.95	77	3.1

(1) Gonzalez-Erico et al, 1979
(2) Juo, 1977
(3) Evans and Kamprath, 1970
(4) Brenes and Pearson, 1973

Table 2 - Critical magnesium saturation for plant growth.

Soil	Crops	Critical Mg Saturation	Range of CEC	Reference
		%	meq/100g	
Ultisols	Sudangrass and Ladino clover	4	3.0-14.0	Adams and Henderson, 1962
Alfisols Ultisols Oxisols	Maize	5	2.6-11.6	Lombin and Fayemi, 1975
Alfisols Ultisols	German millet and Alfalfa	5	8.4-18.8	McLean and Carbonell, 1972

Table 3 - Critical levels of exchangeable K for plant growth.

Area	Soil	Crop	K Critical Level	References
			meq/100g	
Brazil	Oxisols	cotton	<0.10-large response >0.20-little response	Freitas et al., 1966
Hawaii	Oxisols	sugar cane	0.20	Humbert, 1953
Louisiana	Alluvial	sugar cane	0.28	Ricaud, 1965
Alabama	Ultisols low CEC	cotton	0.20	Rouse, 1960
USA	Mollisols	millet-greenhouse	0.20	Barber et al., 1962
USA	Mollisols	corn-field	0.30	Hanway et al., 1962
Texas	Montmorillonite-mica clay soils	grain soybean	0.40	Hipp and Thomas, 1967

Table 4 : Critical soil test levels for extractable soil P.

Soil Test	Region	Crop	Critical Level μg/g soil	References
Bray 1 0.025NHCl + 0.03N NH_4F 1:10 soil/solution shake 5 minutes	Virginia sandy loam	corn	36	Alley and Bertsch (1983)
	Mexico	corn	25	Ortega (1971)
	U.S.A. Midwest soils	corn	30	Thomas and Peaslee (1973)
Olsen 0.5M $NaHCO_3$ 1:20 soil/solution shake 30 minutes	U.S.A. calcareous	wheat	10	Olsen et al (1954)
	India	wheat	11	Gattani and Seth (1973)
	Brazil	corn	6-10	Yost et al (1979)
	Virginia	corn	18	Alley and Bertsch (1983)
Mehlich 1 0.05 N HCl + 0.025 N H_2SO_4 1:4 soil/solution shake 5 minutes	Brazil clay	corn	10-15	Yost et al (1979)
	Alabama clay loam	corn	15	Rouse (1968)
	N. Carolina silty clay loam	corn	8	Kamprath (1967)
	Virginia sandy loam	corn	33	Alley and Bertsch (1983)
	Georgia sandy loam	wheat	27	Hargrove et al (1984)

Table 5 - Critical micronutrient cation levels

Micronutrient	Critical Levels Mehlich 1	 DPTA (1)
	ppm	
Zinc	0.8 (2)	0.8
Copper	0.3 (3)	0.2
Manganese	4.7-9.7 (4)	1.0
Iron	-----	4.5

(1) Critical values given by Lindsay and Norvell
(2) Cox and Wear, 1977
(3) Makarim and Cox, 1983
(4) Mascagni and Cox, 1985

Table 6 - Soil Fertility modifiers used in the FCC system. (Adapted from Sanchez et al., 1982).

FCC modifier	Soil depth cm	Definition
e = low CEC	20	CEC <4 meq/100g, $\sum$ bases + exch Al or <7 meq/100g, $\sum$ cations at pH 7
a = aluminium toxicity	50	> 60% Al saturation of effective CEC or 67% acidity saturation of CEC pH 7
h = acid	50	10-60% Al saturation of the effective CEC
b = basic reaction	50	Free $CaCO_3$ or pH > 7.3
k = low k reserves		$<10\%$ weatherable minerals in silt and sand fraction: or exch. K < 0.2 meq/100g
i = high p fixation by iron		% free Fe_2O_3/% clay >0.15 and more than 35% clay or hues of 7.5 YR or redder, granular structure and >35% clay

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COMPARISON OF SOIL EXTRACTION BY 0.01 M $CaCl_2$, BY EUF AND BY SOME CONVENTIONAL EXTRACTION PROCEDURES *)

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I Introduction

In soil testing laboratories, soil samples are analysed to predict nutrient availability for agricultural production. Since large numbers of samples must be processed quickly and efficiently, these laboratories are interested in simple, uniform extraction procedures. This may explain the interest in methods like Electro-Ultrafiltration (EUF) for the purpose of soil testing. Here one extraction procedure produces a solution which can be used for the determination of a number of soil parameters.

In the present study a comparison is made between the values of extractable quantities of nutrients found:
a) with various extraction procedures used nowadays in the Netherlands
b) with the EUF procedure
c) with an 0.01 M $CaCl_2$ extraction procedure.

II Materials and methods

In this study 20 soils were used: 4 reclaimed peat subsoils, 6 sandy soils, 9 clay soils and 1 loess.
The EUF method has been described by Nemeth (Nemeth, 1985). The characteristics of the standard procedures used in the Netherlands are given in table 1.

Table 1. Standard procedures for soil testing in the Netherlands

Parameter	Extracting solution	Remarks
pH	1 M KCl	1:5 v/v; air-dry soil
K, Na	0.1 M HCl and 0.02 M $H_2C_2O_4$	1:10 w/v; air-dry soil
Mg	0.5 M NaCl	1:20 w/v; air-dry soil
P	water	1.2 ml of air-dry soil is incubated with 2 ml water at 20°C for 22 hours. Next 70ml of water is added and P is extracted
N-min (NO_3+NH_4)	0.5 M NaCl or 0.5 M KCl	1:2.5 w/v; field-moist soil

For the extraction with 0.01 M $CaCl_2$, 10 g sample air-dry soil was shaken for two hours at 20°C with 100 ml $CaCl_2$ solution. First the pH was measured. After centrifuging the following determinations were made in the supernatant:
- Na and K: flame atomic emission spectrometry (FAES)
- Mn and Mg: flame atomic absorption spectrometry (FAAS)

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*) This contribution is a short version of a paper with the same title in Plant and Soil (Houba e.a., 1986).
Copies are available from the authors of from the Labex Secretariat.

- P: colorimetrically as molybdenum blue .
- NO_3: colorimetrically after reduction to NO_2 as alpha-naphtyl-amine-paradiazobenzene-parasulphonic acid
- NH_4: colorimetrically as indophenol blue
- 'reduced nitrogen' (= soluble organic N plus NH_4-N) as described by Novozamsky et al.(1983).

III Results

Mg:
Almost equal amounts were extracted with 0.5 M NaCl and 0.01 M $CaCl_2$ solutions, which is shown by the relation:

$$\text{Mg-CaCl}_2 = 0.91 \times \text{Mg-NaCl} + 2 \qquad r = 0.976$$

This holds up to 100 mg Mg per kg air-dry soil, which is sufficient for fertilizer advisory purposes.
The values yielded by EUF extractions were consistently lower than those obtained with NaCl.

$$\text{Mg-EUF} = 0.2 \times \text{Mg-NaCl} + 21 \qquad r = 0.770$$

This rather poor relation may probably be ascribed to analytical difficulties encountered with the EUF extraction method.

Mn:
The results with the EUF-method were not reliable. In $CaCl_2$ extracts Mn is better measurable and is in good agreement with the pH values of the soils.

Na:
The relation between the 0.01 M $CaCl_2$ and EUF extracts is very close.

$$\text{Na-CaCl}_2 = 1.0 \times \text{Na-EUF} - 12 \qquad r = 0.993$$

The relatively large intercept is due to Na contamination from the glass cuvettes and filters of the EUF apparatus.

K:
Results show a dependence on soil type.
Sandy soils:

$$\text{K-CaCl}_2 = 0.91 \times \text{K-HCl} - 14.05 \qquad r = 0.950$$

Clay soils:

$$\text{K-CaCl}_2 = 0.3 \times \text{K-HCl} + 21.58 \qquad r = 0.876$$

Such a divergence is to be expected as 0.1 M HCl also extracts a portion of the 'fixed' fraction of K from clay soils.

P:
Comparing the amounts of P extracted with water and with 0.01 M $CaCl_2$, we find less P with $CaCl_2$ as the introduction of Ca ions in the system influences the solubility of the phosphates.
For calcareous soils the relation is:

$$\text{P-CaCl}_2 = 0.14 \times \text{Pw} - 0.52 \qquad r = 0.956$$

For non-calcareous soils the relation is:

$$\text{P-CaCl}_2 = 0.34 \times \text{Pw} - 1.67 \qquad r = 0.886$$

With the EUF method two successive extractions are performed: first 30 minutes at 20°C, followed by 5 minutes at 80°C. The relations are as follows:

$$\text{P- EUF(1st+2nd fraction)} = 2.4 \times \text{Pw} - 4.0 \qquad r = 0.907$$

$$\text{P-EUF(1st fraction)} = 1.2 \times \text{Pw} - 2.5 \qquad r = 0.912$$

$$\text{P-EUF(2nd fraction)} = 1.1 \times \text{Pw} - 1.5 \qquad r = 0.862$$

N:

Next to the inorganic ions NO_3 and NH_4, an additional mobile organic-N fraction is extracted with the EUF procedure. A comparison of the EUF-N values of the first fraction with those of total soluble N in 0.01 M $CaCl_2$ extracts leads to the following relation:

$$\text{Total-N}(CaCl_2) + 1.04 \times \text{EUF-N(1st fraction)} - 5 \qquad r = 0.82$$

When NO_3 values are compared separately the relation is:

$$NO_3\text{-N}(CaCl_2) = 1.1 \times NO_3\text{-N(EUF)} - 1 \qquad r = 0.96$$

It should be pointed out that the EUF values are poorly reproducible.
The amount of nitrogen recovered in the second EUF fraction falls within the experimental error range and is further not considered.

IV Conclusions

The analytical results for various soil nutrient parameters obtained with the $CaCl_2$ extraction procedure compared generally well with those obtained with two established procedures in use for making fertilizer recommendations. The Electro-Ultrafiltration technique did not supply more useful information than did the Dutch standard procedure except for K, for which nutrient the EUF procedure can differentiate between readily exchangeable and fixed fractions. A drawback of EUF is the poor reproducibility.
The $CaCl_2$ procedure has the advantage of low cost and of uniformity in extraction procedure for a range of soil fertility parameters.

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DISCUSSIONS AND RECOMMENDATIONS

I Introduction

At the workshop the presentation of each paper was followed by a brief discussion. Although for the general discussion parallel sessions were planned, each covering a specific analysis or other problem, the workshop attendants preferred to have plenary meetings in order to be involved in all topics. In the workshop programme (annex I) the chairmen of the sessions are mentioned. The recommendations were drafted by J.M. Kimble, L.P. van Reeuwijk and L.K. Pleijsier. The following is an amalgamation of the discussions following the papers, of the discussion sessions on specific topics and of the discussions on the draft recommendations. A division has been made in topics on the LABEX programme and topics on the specific soil analyses.

II On the programme

1. Aims

The Labex programme was initiated on recommendation of the 2nd International Soil Classification Workshop in 1978. It had become clear at that moment that international classification and correlation of soils was hampered by great variability in analytical data resulting from the poor standardization of analytical methods. Therefore the Labex programme was to start a laboratory cross-checking programme with the aim to investigate the possibilities of standardization. For each relevant soil parameter a universal analytical procedure was to be established that could be incorporated in international soil classification systems.

The discussions during the workshop made it clear that the participating soil laboratories are in the first place very interested in a check on the quality of their own performance with their present procedures. An improved quality should become apparent in a reduced bias in the analytical data of different laboratories (the results getting closer). Comparison of data is made easier by uniformity of methods, therefore the quality control can not be seen as something completely different from the original objective of the programme. Thus, the reconsideration of the aims entails a mere shift in emphasis. A 'standard method' is needed for mutual comparison of analytical results, but for regular use the participating laboratories might continue to develop, modify and use procedures suiting their own needs.

A long term goal is to develop procedures which have less variability and can be run with a minimum of equipment and capital expense. The Labex programme should not limit itself to soil characteristics needed for soil classification and correlation, but widen its scope and particularly include soil fertility parameters.

2. Continuation

All workshop attendants were strongly in favour of a continuation of the programme. Mention was made of at least a 5 year, if not 10 year period.
To reduce the wide variability of the analytical data that exists at present improvement of the quality of the laboratory performance of the participants is needed and this is a time consuming affair.
The quality control of individual laboratories appears to be in high demand (c.f. the plant analysis programme).
The Labex programme is also a stimulus of awareness of the intra laboratory performance and the need for standardization of methods and procedures.

3. Status

At present Labex is an association of soil laboratories cooperating on a voluntary basis, aiming to improve their quality of work.

The International Standard Organization (ISO) has recently established a Technical Committee (TC) on soil quality. This ISO-TC consists of representatives from interested national standardization institutes. Its aim is to set standards of soil quality parameters to improve international exchange of data. To maintain a liaison with this ISO-TC the International Society of Soil Science (ISSS) has established a Standing Committee. Labex will inform both the ISO and ISSS on the outcomes of the workshop and advise the Labex participants on ISO developments.

Possibly Labex could become a (Provisional) Working Group under the mentioned ISSS Standing Committee. At the next ISSS International Congress in Japan in 1990 a special session could be held to present the Labex programme with all accompanying publicity and documentation (a next workshop is planned in 1989 at Wageningen).

Labex participants are encouraged to become active in national normalization committees. Labex may be instrumental in the exchange of information between national soil laboratory networks. The key labs in the national programmes should therefore be included in Labex.

4. Financing

The present phase of the programme is financed from a grant from the Dutch Government Directorate for Technical Cooperation. This grant will expire on 1st July 1987. Considering that without co-funding the continuation of this subsidy is doubtful, all participants are urged to pursue the possibilities for this. Options are:

a) appeal to selected donor agencies by groups of developing country participants;
b) subscription fee;
c) assistance-in-kind (training, servicing of equipment, other forms of direct support to fellow-labex-participants).

Participants could approach UN specialized agencies (UNEP, UNESCO, FAO), or the agricultural industry (more specifically fertilizer related industries) could be approached.

5. Operation of the continued programme

As many participants experience difficulties in clearing the Labex soil samples from the customs authorities in their country the mailing of sample packages will be limited to once a year. The possibility of sterilization of soil material by gamma radiation will be investigated.

The samples and parameters to be analyzed will be differentiated according to region or climate (e.g. calcareous and/or saline soils versus acid and/or strongly weathered soils). Participants can then select which set of samples they wish to receive. Also a choice can be made which parameters they will analyze.

To allow mutual comparison of the data the participants analyze the samples following prescribed standard methods. To assist participants target values will be published. These target values will be obtained from the analytical results from 5 'major' laboratories.

The standard methods should be clearly and concisely written and distributed to all participants for comments. In this way all ambiguities and unclear elements should be removed before the procedure is actually used.

For further comparison each lab should continue to run its usual procedures and report results and identify procedures used. All results will have to be reported in duplicate.
While this quality control is continuing new or improved methods or procedures for selected soil parameters can be tested by a limited number of 'reference' labs. With this testing the critical steps in the procedures will have to be identified. Procedures showing merit are made available to all participants for further testing.
Reference samples will remain available. They can be supplied on demand to any laboratory against charges.

6. Mutual exchange of information

To improve the exchange of information between the Labex participants a newsletter will be started. This will allow asking of questions, exchange of ideas, etc. Individual advice to participants can be provided on request. These requests can be channeled to specialists in the problem field.
The newsletter can also be used to announce courses and individual training offered by participants.

III On the various analyses

1. General

Soil analysis very often is not a total analysis of an element or parameter. In general only a fraction is measured, and the proportion of this fraction of the total value depends on the extraction procedure. Thus, standardization of this extraction procedure is very important. The standard procedure should be clearly and concisely described as indicated in paragraph I.5. To improve the uniformity of the extraction step used by the Labex participants a uniform method of shaking is proposed by use of an end-over-end shaker. This shaker could be of a simple design, that can easily be locally made. A design will be published in the Newsletter.

2. Analyses related to soil fertility

Many parameters involved in soil testing for soil fertility have already been included in the present programme (e.g. exch. bases, CEC, pH, texture, exchangeable acidity). For other parameters numerous analytical methods exist. Attention in first instance should be given to phosphorus. Suggested procedures are:
- Bray 1
- Olsen
- Mehlich 1
- Modified Olsen (Dabin, ORSTOM)
- own procedure

Of the first four methods the detailed procedures will be distributed.
The emphasis will be on the quality control aspect rather than developing new methods. Also aspects of interpretation of data and fertilizer recommendations will not be considered by Labex. There exists also a strong interest in P-retention capacity. Alternative methods are: Blakemore/ Japanese method/ North Carolina method. Suggestions for other alternatives are invited.
Micronutrients will not be included for the time being.

3. Cation Exchange Capacity

As standard procedure NH_4-Acetate, pH 7 will be used for the time being. Equivalent variations of this procedure will be provided by USDA-SCS National Soil Survey Laboratory, Lincoln, Nebraska, USA and distributed by Labex. In addition, for saline and calcareous soils the Na-Ac, pH 8.2 can be used.
Newly proposed procedures (AgTU, Co-hexammine, choline chloride, Li(Ba)EDTA) will be tested by a limited number of labs. Based on this testing recommendations will be made for further testing and/or possible substitution for the Amm.Aetate method. Effective Cation Exchange Capacity (ECEC) will be determined. ECEC has been defined as sum of exchangeable bases and exchangeable acidity.
Exchangeable acidity is Al + H measured by titration of a 1 M KCl extract. Exchangeable Al should be measured in extract along with exchangeable acidity.

4. Particle Size Distribution

Equivalent procedures (including all steps for complete analysis) for pipette and hydrometer will be distributed.
In these procedures the (optional) pretreatments and their sequence are as follows:
- removal of organic matter
- removal of carbonates
- deferration

The dispersing agent will be sodiumhexametaphosphate buffered with Na-carbonate.
For mechanical dispersion the end-over-end-shaker as mentioned in paragraph III.1 will be used. Laboratories having proposals for new and/or improvements to existing procedures are encouraged to submit them for inclusion in the Newsletter. Especially ways of speeding up the pipette method are much in demand by participants.

5. Organic Carbon

It appears that most participants use the Walkley-Black procedure (or a related one). A number of participants use procedures which supposedly give 100% recovery. This combination should allow an evaluation of the former procedure. Suitable samples will be distributed for comparison. Results should be submitted without use of correction factors. The correction factor normally used by participant should be reported.

6. pH

In addition to pH-H_2O either pH-KCl (1M) or pH-$CaCl_2$ (0.01M) or both should be run (1:2.5).
Also the pH of the distilled water used should be reported.

7. Salt affected soils

Standard procedures will make use of saturation extract and 1:5 extract. The following ions in the extract should be run: Ca, Na, Mg, K, SO_4, Cl, (NO_3), HCO_3 and CO_3.
pH to be measured in saturated paste. EC to be measured in extract.

8. Other parameters considered for inclusion

1) Carbonates
2) Gypsum
3) Aggregate stability
4) Water dispersable clay
5) 15 bar water retention and/or moisture equivalent
6) Extractable acidity (pH 8.2)
7) Dithionate Fe, Al and Mn
8) Oxalate Fe, Al, Si, Mn and PO_4
9) Pyrophosphate Fe and Al
10) Sulfur (Sulfate) Ca-phosphate extractable.

ANNEX I

Workshop Programme

Monday 25 August
morning : Arrival of participants
afternoon: Introductory session; Chairman: W.G. Sombroek.
Welcome by W.G. Sombroek, Director ISRIC.
The Labex programme and its results sofar: L.K. Pleijsier.
Sources of analytical variability in soil chemical analyses: J.D. Etchevers.
Interlaboratory cross-checking in Argentina: H.J.M. Morras.
The International Plant Sample Exchange: V.J.G. Houba, I. Novozamsky and J.J. van der Lee.

Tuesday 26 August
morning: CEC analysis; Chairman: J.D. Etchevers.
On the way to improve CEC analysis in soils: a new comprehensive single-step procedure with Li-EDTA: L.Th. Begheyn.
Use of the AgTU-complex for CEC measurement of soils: J.L. Pleysier.
Kjeldahl, Kjeltec and Auto-analyzer techniques for the determination of CEC of soils: Y.P. Kalra and D.G. Maynard.
Exchangeable Cations - An Australian experience: S. McLeod.
afternoon: CEC analysis (cont.); Chairman: J.J. van der Lee.
Comparison of exchangeable bases and CEC by the cobaltihexammine method and by the standard Ammonium Acetate method on some Malinese soils: M.K. Keita and F. v.d. Pol.
Determination of CEC and exchangeable cations in soils of different climatic regions by the BaCl-TEA- and the Ammonium Acetate method: F. Grueneberg.
General Discussion on CEC.
evening: Discussion session; Chairman: W.G. Sombroek.
Discussion on operational aspects of the programme.

Wednesday 27 August
morning: Other analyses; Chairmen: S. McLeod, Sh. Abdel Aal.
A comparison of 3 procedures used in particle-size distribution analysis of soils: V.J.G. Houba, I. Novozamsky, E.D.M. Mlay, and R. van Eck.
A final step alternative for direct carbon analyses in soils: L.Th. Begheyn.
Discussion on other analyses and their problems.
afternoon: Soil fertility; Chairman: J.L. Pleysier.
Soil fertility capability assessment: E.J. Kamprath.
Soil testing by means of 0.01 M $CaCL_2$: V.J.G. Houba, I. Novozamsky, A.W.M. Huybregts and J.J. van der Lee.
General discussion on soil fertility aspects.

Thursday 28 August
morning: Discussion-session; Chairmen: E. Bornemisza, L.P. van Reeuwijk.
topics: CEC and exchangeable bases.
Texture
afternoon: Discussion-session; Chairman: J.M. Kimble.
topics: Water soluble salts
Organic C
pH
visits to:
- Agricultural University Department of Soil Science and Geology (L.Th. Begheyn)
- Agricultural University Department of Soil Science and Plant Nutrition (V.J.G. Houba).

Friday 29 August

morning: Discussion-session; Chairman: W.G. Sombroek.
Final discussion on workshop recommendations.
Closing and farewell.

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